

Advances in **ORGANOMETALLIC CHEMISTRY**

EDITED BY

F. G. A. STONE

DEPARTMENT OF INORGANIC CHEMISTRY
SCHOOL OF CHEMISTRY
THE UNIVERSITY
BRISTOL, ENGLAND

ROBERT WEST

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

VOLUME 1



1964

ACADEMIC PRESS

New York • London

COPYRIGHT © 1964, BY ACADEMIC PRESS INC.

ALL RIGHTS RESERVED.

NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM,
BY PHOTOSTAT, MICROFILM, OR ANY OTHER MEANS, WITHOUT
WRITTEN PERMISSION FROM THE PUBLISHERS.

ACADEMIC PRESS INC.

111 Fifth Avenue, New York 3, New York

United Kingdom Edition published by

ACADEMIC PRESS INC. (LONDON) LTD.

Berkeley Square House, London W.1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 64-16030

PRINTED IN THE UNITED STATES OF AMERICA

List of Contributors

G. F. EMERSON, *Department of Chemistry, The University of Texas, Austin, Texas*

HEINZ P. FRITZ, *Institut für Anorganische Chemie der Universität München, Munich, Germany*

REYNOLD C. FUSON, *Center for Advanced Study, University of Illinois, Urbana, Illinois*

HENRY GILMAN, *Iowa State University, Ames, Iowa*

HENRY G. KUIVILA, *Department of Chemistry, College of Technology, University of New Hampshire, Durham, New Hampshire*

R. PETTIT, *Department of Chemistry, The University of Texas, Austin, Texas*

GERALD L. SCHWEBKE, *Iowa State University, Ames, Iowa*

F. G. A. STONE, *Department of Chemistry, Queen Mary College, University of London, London, England**

P. M. TREICHEL, *Department of Chemistry, Queen Mary College, University of London, London, England†*

* Present address: Department of Inorganic Chemistry, The University, Bristol, England

† Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Preface

During the past decade the study of organometallic chemistry has grown rapidly. Expansion of this area of scientific endeavor has been fostered by the discovery of several classes of compounds possessing remarkable structures, by the development of valence theory to account both for the existence of these novel compounds and for the nature of carbon-metal bonds in general, and by the growing use of organometallics in industrial processes. Organometallic chemistry now seems well on its way toward establishing its identity as an important domain of science, representing a convergence of inorganic, organic, and physical chemistry where the respective disciplines can benefit by interaction with each other.

In the volumes of this series, which we expect to have published at approximately twelve-month intervals for several years, we plan to include reviews of recent developments in all of organometallic chemistry, broadly defined as the science of substances containing organic groups bonded to metals. Included will be not only discussions of recent advances in the synthesis, properties, and reactions of organometallic compounds, but also articles on the application of modern structural techniques to organometallic problems, and on new technological applications of organometallic substances. We hope that chemists with a general interest in this field will, by turning to these volumes, be able to find recent information about many of the most active areas in organometallic chemistry.

No series of this sort could be successful without the cooperation of authors willing to undertake the demanding task of reviewing their fields of special competence. Users of these volumes, as well as the Editors, owe a debt of gratitude to the many busy scientists who are taking time from other labors to write these articles. The Editors also wish to thank the two members of the editorial advisory board for this series, Professors Henry Gilman and Harry J. Emeléus, whose advice and encouragement, in the initial planning stages, has been of vital importance.

F.G.A.S.
R.W.

January, 1964

Diene-Iron Carbonyl Complexes and Related Species

R. PETTIT and G. F. EMERSON

*Department of Chemistry, The University of Texas,
Austin, Texas*

I. Introduction	1
A. Scope	1
B. Historical Aspects	2
II. Structural Considerations	4
A. Evidence from X-Ray Data	4
B. Other Physical and Chemical Properties	10
III. Preparation and Properties of Diene-Iron Tricarbonyl Complexes	13
A. Preparation	14
B. Chemical Properties of Diene-Iron Tricarbonyl Complexes	28
IV. Related Iron Carbonyl Complexes	30
A. Dienyl-Iron Tricarbonyls	30
B. π -Allyliron Carbonyls	34
C. Monoolefin-Iron Tetracarbonyl Complexes	35
D. Iron Carbonyl Complexes from Fulvenes	36
V. Iron Carbonyl Complexes Derived from Acetylenes	37
A. Introduction	37
B. Complexes from Iron Carbonyl Anions	37
C. Complexes from Substituted Acetylenes and Iron Carbonyls	38
D. Complexes from Acetylene and Iron Carbonyls	41
References	43

I

INTRODUCTION

A. Scope

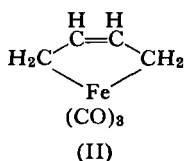
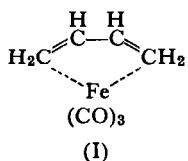
In recent years a large number of compounds have been isolated in which an olefin or some other unsaturated hydrocarbon species is bonded to an iron carbonyl residue. As far as the general type of bonding of the unsaturated ligand to iron is concerned, these materials may be somewhat related to the well-known ferrocenes. However, the chemical behavior of the materials

suggests that a separate classification is justified. The present review does not include compounds which possess the ferrocene-type structural unit. Furthermore, although many of the transition metals other than iron are known to form analogous olefin-metal complexes, the present review is restricted to discussion of the iron complexes. These are certainly the most numerous and varied. It is also apparent that each metal is associated with its own peculiarities as far as chemical properties are concerned and a comprehensive discussion of comparative and speculative chemical behavior of all the related organometallic species is far beyond the aim of this review.

B. Historical Aspects

The olefin-iron carbonyl complexes were first introduced by two entirely different synthetic methods. In 1930 Reihlen and co-workers (1) obtained butadiene-iron tricarbonyl by a reaction of butadiene with iron pentacarbonyl and in 1953 Reppe and Vetter (2) reported organoiron compounds, since shown to be diene-iron carbonyl complexes, following reaction of acetylene with iron carbonyls.

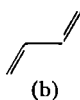
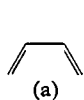
The first workers, while attempting to elucidate the structure of iron pentacarbonyl, treated $\text{Fe}(\text{CO})_5$ with butadiene in a sealed tube at 150°C for several hours and obtained a product which analyzed as $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$. Although they were not able to assign a definite structure to this material they considered that the iron atom was bonded to the terminal carbon atoms of the diene and to three carbonyl groups. The cyclic structure (I) was proposed; however, they stated that the alternative structure (II) could not be ruled out.



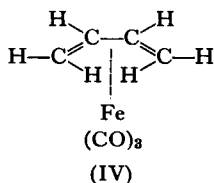
They also obtained organoiron complexes with isoprene and $\text{Fe}(\text{CO})_5$ but the reaction apparently failed in the case of isobutylene.

Apart from a patent (3) which appeared in 1947 no further work was published on this particular reaction until Hallam and Pauson (4) extended the study in 1958. These latter workers investigated further the product obtained from butadiene and $\text{Fe}(\text{CO})_5$. The diene complex was found to resist hydrogenation and not to undergo Diels-Alder-type reactions. Ozonolysis

of the material was found to produce some formaldehyde while vigorous reaction with LiAlH_4 led to the formation of some butadiene. This, together with some spectroscopic evidence, led them to suggest that the butadiene molecule remained essentially intact in the organoiron complex. Furthermore, they showed that an analogous compound, 1,3-cyclohexadiene-iron tricarbonyl, could be prepared in a similar manner from 1,3-cyclohexadiene and $\text{Fe}(\text{CO})_5$. They therefore concluded that the diene system adopted a *cis* arrangement of double bonds as in (IIIa), rather than a *trans* one (IIIb) within the complex. The structure then proposed is shown by formula (IV).



(III)



The butadiene moiety in (IV) is presumed to be planar, or nearly so, and the iron atom lies below this plane and approximately equidistant from the four carbon atoms of the diene system. The nature of the diene-iron bonding was presumed to involve interaction of the Fe atomic orbitals with π molecular orbitals of the diene system as a whole and was therefore more analogous to the π bonding in ferrocenes, rather than the σ type implied in Reihlen's structure (II). The conjugated nature of the diene system was considered to be an essential feature necessary for the formation of iron derivatives of this type.

At about the same time Hallam and Pauson published their work, the recognition of the diene- $\text{Fe}(\text{CO})_3$ grouping as a stable system was independently made by several groups of workers who were then extending the field introduced by Reppe and Vetter (5-10). The chemistry associated with the reactions of acetylene is, by and large, an entity in its own and, for convenience, we have retained this separation in our discussion.

Since 1958 a considerable amount of research activity has centered around these systems, both in the acetylene-iron carbonyl reactions and the direct reactions of olefins with iron carbonyls. The types of unsaturated ligands which are now known to occur in stable iron carbonyl complexes include substituted and nonsubstituted cyclic, acyclic, and nonconjugated dienes as well as some aromatic systems. Furthermore, what may be formally regarded as dienyl cations as well as allyl cations and radicals are found to

occur as ligands in certain stable iron carbonyl systems. Heterocyclic diene-iron carbonyl complexes are now known and several monoolefin-iron tetracarbonyl complexes have also recently been reported. Finally, more complex systems, possessing two or more iron atoms per molecule, are now well known.

II

STRUCTURAL CONSIDERATIONS

A. Evidence from X-Ray Data

Until recently, the electronic structure proposed by Hallam and Pauson for the diene-iron tricarbonyl complexes seems to have been generally accepted. However, since 1960, several significant X-ray studies have been

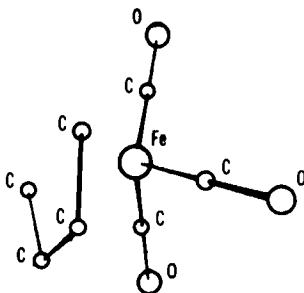


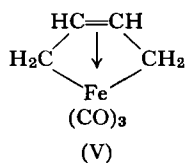
FIG. 1. The structure of butadiene-iron tricarbonyl, after Mills and Robinson. The bond lengths of the C—C bonds are 1.45 and 1.46 Å.

made which tend to indicate that the nature of the bonding is more complex than this. Mills and Robinson (11) in 1960 first published the X-ray data obtained for butadiene-iron tricarbonyl. The salient features of this study are given in Fig. 1.

The carbon atoms of the butadiene are found to be *cis* and coplanar. The bond angles are 118° for $C_1-C_2-C_3$ and approximately 70° for $Fe-C_1-C_2$. The iron atom lies below the plane of the diene carbon atoms and is approximately equidistant (2.1 ± 0.04 Å) from these four carbons. The plane of the butadiene carbons is not quite parallel to that defined by the three carbon atoms of the carbonyl groups. These data certainly tend

to support Hallam and Pauson's formulation over that of the two possible structures mentioned by Reihlen and co-workers.

It should be mentioned at this point that in 1959 Green and co-workers (12) introduced another interesting structure for butadiene- $\text{Fe}(\text{CO})_3$. These workers found that the NMR spectrum of butadiene-iron tricarbonyl displayed two clearly different proton types. Four of the hydrogens appeared in the region of aliphatic hydrogens while the remaining two protons appeared at lower fields nearer the region of normal olefinic hydrogens. This data suggested structure (V).



The same authors pointed out, however, that the infrared stretching frequencies of the C—H bonds were more like those associated with sp^2 rather than with sp^3 hybridized carbon-hydrogen bonds. In view of the unknown effect the $\text{Fe}(\text{CO})_3$ grouping might have on the local magnetic field in the diene moiety they considered the infrared evidence, favoring (IV), to be more diagnostic.

Dickens and Lipscomb, in 1961, obtained the X-ray data for cyclooctatetraene-iron tricarbonyl (13, 14) and cyclooctatetraene-diiron hexacarbonyl (14, 15). These two complexes, which will be discussed again in a later section, had aroused considerable interest and speculation concerning the structural features. Chemical evidence for the first of these had indicated no free olefinic double bonds to be present and NMR data indicated only one type of hydrogen present and it was widely assumed that the C_8H_8 ring in this complex was planar rather than having the tub conformation present in the free hydrocarbon. Two molecular orbital calculations, using symmetry orbitals based upon a planar configuration of the C_8H_8 ring, had purported to have rationalized the chemical binding of the complex (16, 17).

However, the X-ray data showed clearly that, in the crystalline state at least, the $\text{Fe}(\text{CO})_3$ grouping is attached to the C_8H_8 ring through a diene unit rather than a tetraene.

The structure found by X-ray studies is shown in Fig. 2.

The C_8H_8 ring is found to lie in two planes, the angle between them being 41° . From the interatomic distances it is clearly seen that the $\text{Fe}(\text{CO})_3$ group

is associated with only one pair of conjugated double bonds with the remaining pair forming a second plane and having relative positions very similar to those in butadiene. The iron atom is at about the same position with respect to the four carbons of the diene unit to which it is bonded as was reported for the butadiene complex, though it possibly lies closer to the central carbons of the diene. The carbon-carbon distances involved in the coordinated diene unit are again equal though a little shorter than those found in the butadiene complex.

On the basis of the size of overlap integrals of various orbitals of the atoms having these relative positions Dickens and Lipscomb considered

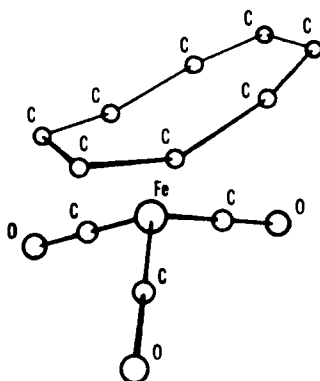


FIG. 2. The structure of cyclooctatetraene-iron tricarbonyl, after Dickens and Lipscomb. The C—C bond distances of the diene-Fe(CO)₃ unit are each 1.42 Å.

that both structural types, (IV) and (V), appeared reasonable, with some bias in favor of the latter. The true structure, they thought, might lie somewhere between these two representations.

The second complex, $C_8H_8Fe_2(CO)_6$, had also aroused considerable speculation concerning its structure (16–21), all of which was shown to be incorrect. The pertinent data of the X-ray studies are shown in Fig. 3.

The main point here is that the C_8H_8 ring adopts a chair conformation in the complex with each iron atom again clearly associated with a diene unit. In this conformation little π -type interaction is to be expected between the two diene units bonded to iron. It is also of interest that the disposition of the three carbonyl groups about each iron atom is the same as observed in the earlier studies.

Recent experiments involving the Mössbauer resonance of the two iron

atoms in this complex are in agreement with the X-ray studies insofar as the two iron nuclei are found to be equivalent. Furthermore a similarity in chemical environment of the two iron atoms with that in the $C_8H_8 \cdot Fe(CO)_3$ complex is also suggested (22).

Similar results have been found by Smith and Dahl who showed, from X-ray studies, that in the complex 2,4,6-triphenyltropone-iron tricarbonyl the tropone ring was no longer planar (23). The arrangement of the atoms of the tropone ring and the $Fe(CO)_3$ are as shown in Fig. 4.

It is clear again that the $Fe(CO)_3$ group is attached to a diene unit rather than to the fully conjugated ring as a whole, as might have been anticipated

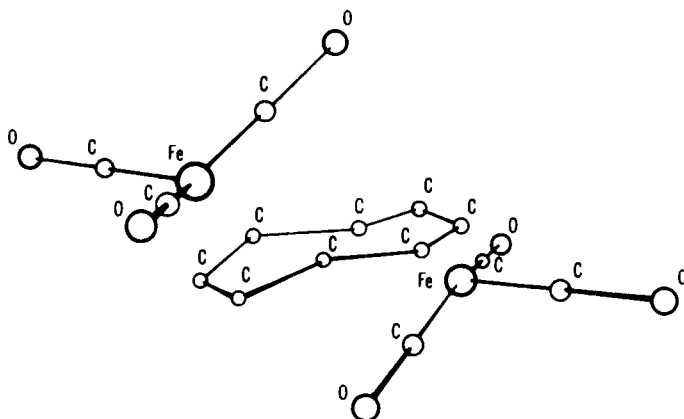


FIG. 3. The structure of cyclooctatetraene-diiron hexacarbonyl, after Dickens and Lipscomb. The C—C bond distances of the diene- $Fe(CO)_3$ units are 1.44, 1.40, and 1.44 Å.

from molecular orbital considerations (24). The two planes of the tropone ring are found to intersect at an angle of 139° . Of particular significance in this study is the fact that carbon atom number 4 (see Fig. 4) is found not to lie in the plane of the three other carbon atoms to which it is attached, but is displaced from this plane by approximately 0.22 Å. This is almost one-half the distance it would be displaced if C_4 were a normal sp^3 hybridized carbon atom. Carbon atom number 6 on the other hand does lie in the plane defined by the three carbon atoms to which it is attached.

On the basis of these results Smith and Dahl proposed that the distorted octahedral-type structure (VI) was preferred as a representation, provided that recognition was made of the contribution provided by structure (VII) to the actual electronic state of the molecule.

It is clear from the foregoing that the diene- $\text{Fe}(\text{CO})_3$ unit is a stable entity of rather complex electronic character. If a third double bond be present in the system then this will not be involved in bond formation to iron. There still remains the question as to which of the two structures, (IV) or (V), is the best mode of representation. On this point the X-ray data are not entirely

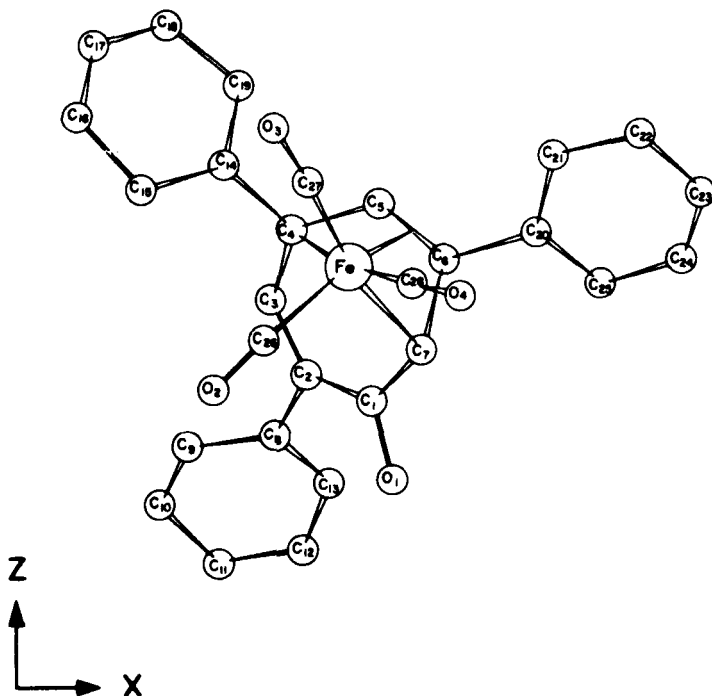
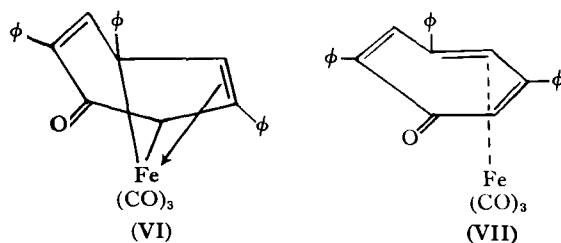


FIG. 4. The structure of 2,4,6-triphenyltropone-iron tricarbonyl, after Smith and Dahl. Some bond distances are $\text{C}_4\text{—C}_5$, 1.45 Å; $\text{C}_5\text{—C}_6$, 1.38 Å; and $\text{C}_6\text{—C}_7$, 1.49 Å.

consistent with the latter type. For example, in Table I the terminal carbon-adjacent carbon bond lengths are listed and compared with those expected in the two cases of an sp^2 hybridized carbon or an sp^3 hybridized carbon being terminal in the diene unit. This particular set of data would seem more to support structure formulations of type (IV).

It is significant too that certain nonconjugated dienes, for example bicycloheptadiene, also form iron tricarbonyl complexes in reactions with $\text{Fe}(\text{CO})_5$ similar to those mentioned. The compound (VIII) is comparable

in physical and chemical properties, including thermal stability, to the complexes of conjugated dienes. A structural formulation of the type (IV) offers the most reasonable sort of bonding to iron in this case, and might suggest



that too strong an emphasis should not be placed on type (V) structures in the conjugated diene complexes.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED^a BOND DISTANCES BETWEEN TERMINAL CARBONS OF DIENE-IRON TRICARBONYLS AND ADJACENT CARBONS OF SUBSTITUENT GROUPS

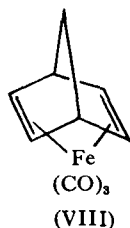
Compound	Bond lengths found (Å)	Bond lengths calculated (Å)	
		<i>sp</i> ² terminal C	<i>sp</i> ³ terminal C
(CO) ₃ FeC ₈ H ₈ Fe(CO) ₃ ^b	1.49	1.48	1.54
C ₈ H ₈ Fe(CO) ₃ ^b	1.45	1.48	1.52
C ₂₅ H ₁₈ OFe(CO) ₃ ^c	1.44	1.48	1.52

^a Values from Dewar (24a).

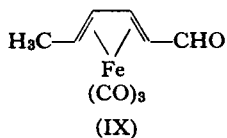
^b Ref. (14).

^c Ref. (23).

Another argument in favor of structure (IV) is suggested by the fact that in certain compounds there is evidence to show that conjugative effects may be readily transmitted through a terminal carbon atom of a diene-iron

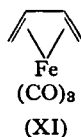
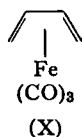


tricarbonyl group. The 2,4-dinitrophenylhydrazone of *trans-trans*-sorb-aldehyde-iron tricarbonyl (IX) is violet-red in color, having a λ_{\max} in the UV region at 392 $m\mu$ (25).



This is typical of dinitrophenylhydrazones of conjugated ketones and, in fact, this absorption occurs at even longer wavelengths than that shown by the uncomplexed sorbaldehyde derivative (386 $m\mu$). Dinitrophenylhydrazones of nonconjugated ketones and aldehydes show maxima in the region 349–363 $m\mu$ (26). Thus for this property at least, type (IV) formulae again appear more illustrative. Other examples of the conjugating ability of the diene-iron tricarbonyl group will be seen in later discussion.

In summary, the detailed nature of the electronic distribution in the diene-iron tricarbonyl structure remains unclear and the mode of representation of the system is therefore somewhat arbitrary. Henceforth in this review we shall use the representation shown by formula (X) for the case



of butadiene-iron tricarbonyl. In some instances, especially when it is desirable to indicate which double bonds in a polyene complex are coordinated, formulas such as (XI) are found useful. Hydrogen atoms will not normally be drawn. In each case the concept of forward coordination from the π orbitals of the olefin and back donation from the iron atom to the antibonding orbitals of the ligand is presumed to apply.


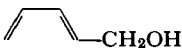
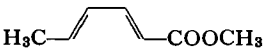

B. Other Physical and Chemical Properties

1. Infrared Absorption

There exists an interesting correlation between the electronic structure of the ligand and the stretching frequencies of the carbonyl groups for a series of diene-iron tricarbonyl complexes. Thus it has been noted by several authors (27, 28) that cationic ligands shift the $C\equiv O$ frequencies to higher

values. It seems possible to extend the correlation further. In butadiene-iron tricarbonyl itself there appear two regions of carbonyl absorption, a narrow intense band at 2053 cm^{-1} and a broader band which is resolved into two maxima at 1985 and 1975 cm^{-1} (29). In analogous derivatives the gross structure of these bands is retained; however their positions shift according to the nature of the ligand. The series of complexes may be divided into the groups shown in Table II. It is seen that the higher the energy of the

TABLE II
INFRARED DATA FOR THE STRETCHING FREQUENCIES OF CARBONYL GROUPS IN DIENE-IRON TRICARBONYL COMPLEXES

Nature of ligand	Representative type	Centers of carbonyl absorption bands (cm^{-1})	
		Narrow band	Broad band
1. Nonconjugated dienes		2035	1967
2. Conjugated dienes with inert substituents		2054	1989 1978
3. Conjugated dienes with strongly electron-withdrawing substituents		2066	2000 1985
4. Carbonium ion type ligands		2120	2072

antibonding orbitals in the organic ligand (estimated by simple Hückel theory) the lower the stretching frequency of the carbonyl groups. Thus the nonconjugated diene, presumed to have the molecular orbitals of ethylene, exhibits the lowest carbonyl frequency of absorption, whereas the cyclohexadienyl cation, at the other extreme as far as vacant molecular orbitals are concerned, shows the highest carbonyl absorption frequencies. These shifts may be qualitatively interpreted in terms of back donation; the lower the vacant orbitals of the ligand, the greater the donation from the iron will be, and the electron density in the antibonding orbitals of the carbonyl group will be at the same time diminished, giving rise to a stronger $\text{C}\equiv\text{O}$ bond.

2. Nuclear Magnetic Resonance Absorption

As mentioned earlier, a precise interpretation of the NMR spectrum of butadiene-iron tricarbonyl is rendered difficult because of the unknown effects of the iron tricarbonyl group upon the shielding of the protons on the ligand. Nevertheless, the spectra of a fairly large number of compounds have now been studied and certain patterns can be seen which can be of considerable utility in assigning a structure to an unknown compound.

Reported first by Green and co-workers (12) the protons in butadiene-iron tricarbonyl fall into two widely separated regions, the two central protons appearing at low field with respect to the terminal ones. In cyclic dienes (XII), the protons on the central carbons of the diene system (C_2 and C_3) lie




in the region $4.6\text{--}4.9\tau$. The only significant exception known is in the case of 2,4-bicyclo[5.1.0]octadiene-iron tricarbonyl (30, 31) where these protons are reported to lie at 5.49τ . The terminal protons, which in cyclic systems are necessarily *syn* to hydrogen atoms on the central carbons, vary more in position, lying at $6.6\text{--}7.3\tau$.

The central protons in the acyclic complexes (XIII) lie in the region $4.6\text{--}4.9\tau$ when saturated substituents are present (32). A substituent with an unsaturated group, e.g., phenyl or formyl, on a terminal carbon can move the absorption of the adjacent central proton, presumably by deshielding, down to the region $4.0\text{--}4.6\tau$.


Characteristic variations also occur in the position of the terminal protons in the acyclic systems. A molecule having no substituent on C_1 or C_2 will show the *anti* hydrogens on C_1 to be in the region $9.5\text{--}9.8\tau$ and the *syn* hydrogens at $8.2\text{--}8.4\tau$. Saturated substituents at C_1 will move an *anti* hydrogen on C_1 down slightly ($8.9\text{--}9.4\tau$) while unsaturated substituents lower it further still. In the only case so far known of a substituent in an *anti* position on C_1 (*cis*-1,3-pentadiene-iron tricarbonyl) the *syn* proton was significantly lowered to 7.3τ , a position similar to that observed for the corresponding proton in cyclic systems (32).

The anomalous case of the cyclooctatetraene-iron tricarbonyl complex,

3. The Electronic Properties of the Diene-Iron Tricarbonyl Group

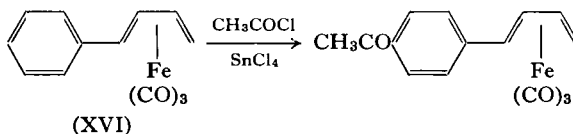


(XIV)



(XV)

The electron-donating properties of the diene-iron tricarbonyl group is also indicated by the fact that phenylbutadiene-iron tricarbonyl (XVI) can be acylated with CH_3COCl and SnCl_4 under mild conditions to give the corresponding *para*-substituted complex (32).



The information available at present is too scanty to determine the relative magnitude and character, i.e., inductive or mesomeric, of this electronic property of the system.

111

PREPARATION AND PROPERTIES OF DIENE-IRON TRICARBONYL COMPLEXES

The greatest majority of diene-iron tricarbonyl complexes have been made by direct action between dienes and one of the three common iron carbonyls

[$\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$], either by simply heating the reagents together or by means of a photochemical combination. In synthesis using $\text{Fe}(\text{CO})_5$ a temperature of 120–160°C is required and therefore sealed systems are necessary for the reactions involving low molecular weight dienes. Reaction times ranging from a few hours to several days are required. Equivalent reactions using $\text{Fe}_3(\text{CO})_{12}$ in an inert solvent such as benzene or ethylcyclohexane give satisfactory yields of products in shorter times and at somewhat lower temperatures (60–120°C).

With $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_{12}$ the products isolated are, with very few exceptions, diene-iron tricarbonyls. However, using $\text{Fe}_2(\text{CO})_9$ with dienes and monoolefins it is possible to obtain olefin-iron tetracarbonyl complexes, discussion of which will be deferred until later.

A. Preparation

1. Conjugated Diene- $\text{Fe}(\text{CO})_3$ Complexes

The simple derivatives of butadiene which have been converted to the corresponding $\text{Fe}(\text{CO})_3$ complexes, utilizing the direct reaction with either $\text{Fe}(\text{CO})_5$ or $\text{Fe}_3(\text{CO})_{12}$, are listed in Table III.

In addition, 1,3-cyclohexadiene (4) and 1,3-cycloheptadiene (27, 40) react to give the analogous complexes. All of the complexes are low-melting crystalline solids or liquids at ambient temperatures; they may vary in color from pale yellow to deep orange. The complexes are thermally stable though a slow decomposition may occur on prolonged exposure to air.

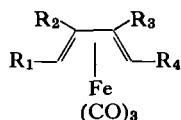
There exists a limitation to this direct method of synthesis in the case of acyclic dienes having *cis*-alkyl substituents. Although these compounds may give rise to diene- $\text{Fe}(\text{CO})_3$ complexes, the ligand in the complex invariably involves a rearranged diene and, as of now, no *cis*-substituted acyclic diene appears to have been prepared by the direct reaction. For example, 2,5-dimethyl-2,4-hexadiene (XVII) reacts with $\text{Fe}(\text{CO})_5$ to give *trans*-2,5-dimethyl-1,3-hexadiene-iron tricarbonyl (XVIII) (41). Likewise, 4-methyl-1,3-pentadiene (XIX) gives *trans*-2-methyl-1,3-pentadiene-iron tricarbonyl (XX) and *cis*-1,3-pentadiene gives *trans*-1,3-pentadiene-iron tricarbonyl (XXI) (42).

The first two of these reactions obviously involve a hydrogen migration, while the last example would appear to be a case of simple geometrical inversion.

Analogous hydrogen migrations are also seen in reactions of several

nonconjugated dienes with formation of conjugated diene-Fe(CO)₃ complexes. For example, 1,4-pentadiene upon reaction with either Fe(CO)₅ or Fe₃(CO)₁₂ gives compound (XXI) (34).

TABLE III
IRON TRICARBONYL COMPLEXES OF BUTADIENE DERIVATIVES

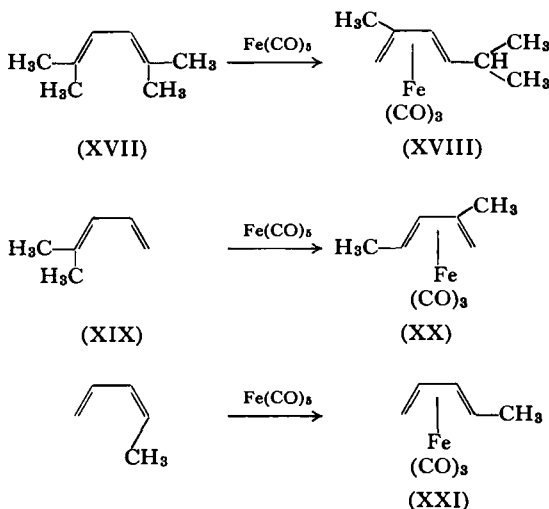


Substituent				
R ₁	R ₂	R ₃	R ₄	Reference
H	H	H	H	(1, 4, 12)
CH ₃	H	H	H	(34)
H	CH ₃	H	H	(34)
C ₆ H ₅	H	H	H	(35)
C ₆ H ₅	H	H	C ₆ H ₅	(36, 35)
CH ₃	H	H	CO ₂ C ₂ H ₅	(34)
CH ₃	H	H	CO ₂ H ^a	(32)
CH ₃	H	H	CONH ₂	(38)
CH ₃	H	H	COCH ₃	(34)
CH ₃	H	H	CN	(34)
CH ₃	H	H	CHO	(34)
CH ₃	H	H	CH ₂ OH	(37)
H	H	H	CH ₂ OH	(37)
C ₆ H ₅	H	H	C ₆ H ₅ —Cr(CO) ₃	(36, 35)
H	H	H	C ₆ H ₅ —Cr(CO) ₃	(35)
C ₆ H ₅ —Cr(CO) ₃	H	H	C ₆ H ₅ —Cr(CO) ₃	(35)
H	C ₅ H ₄ Mn(CO) ₂	C ₅ H ₄ Mn(CO) ₃	H	(35)
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	(38, 39, 12)

^a Obtained by hydrolysis of the ester.

Likewise, 1,4-cyclohexadiene gives 1,3-cyclohexadiene-Fe(CO)₃ (43) and 1,4-dihydromesitylene also gives a 1,3-diene complex (34). Products involving similar rearrangements of a more intensive nature are seen in the 1,3-diene-Fe(CO)₃ complexes formed from 1,5-hexadiene, 4-vinylcyclohexene, and *dl*-limonene (dipentene) (43).

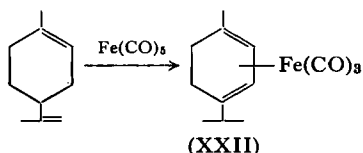
1,5-Cyclooctadiene, when heated with $\text{Fe}(\text{CO})_5$, does not produce an iron carbonyl complex but becomes quantitatively isomerized to 1,3-cyclooctadiene (43). A compound of formula $\text{C}_8\text{H}_{12}\cdot\text{Fe}(\text{CO})_3$ has been obtained from 1,5-cyclooctadiene and either $\text{Fe}_3(\text{CO})_{12}$ in benzene (34) or with $\text{Fe}(\text{CO})_5$ in the presence of sunlight (44); this material is thought to be a 1,5-diene- $\text{Fe}(\text{CO})_3$ complex though, in view of the above rearrangements, it may well prove to be 1,3-cyclooctadiene- $\text{Fe}(\text{CO})_3$. The complex is found



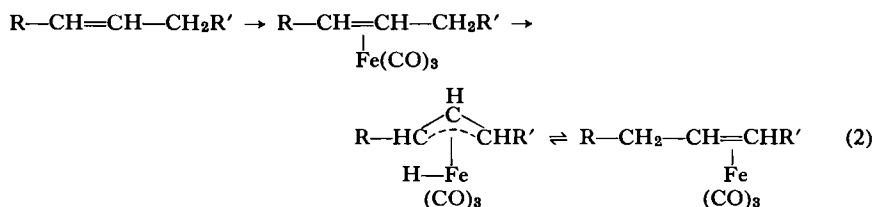
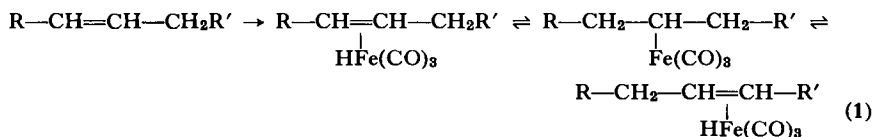
to be thermally very unstable, which could be explained equally well on the basis of its being a nonconjugated ligand or because there exists conformational strain in the 1,3-cyclooctadiene ring when the four unsaturated carbon atoms are held in one plane. It is perhaps significant that 1,3-cyclooctadiene- $\text{Fe}(\text{CO})_3$ cannot be made by the direct reaction of iron carbonyl with the 1,3-diene (43) whereas the 1,3-cycloheptadiene and 1,3-cyclohexadiene complexes can be made in this manner.

It is of interest that reaction of *d*-limonene with $\text{Fe}(\text{CO})_5$ gives an α -terpinene- $\text{Fe}(\text{CO})_3$ complex (XXII) in which no optical activity is retained (42). It is clear from structural considerations that unsymmetrically substituted diene- $\text{Fe}(\text{CO})_3$ complexes should exist in optically active forms and the reason why the product (XXII) is inactive is not immediately apparent. It is likely that the complex (XXII) has also been obtained from dipentene (*d,l*-limonene) and $\text{Fe}_3(\text{CO})_{12}$ (45).

It is relevant to a discussion of possible mechanisms of these rearrangements to note that iron carbonyls can react with monoolefins to cause extensive isomerization of the double bond. Asinger and Berg (46) showed that heating 1-dodecene with $\text{Fe}(\text{CO})_5$ led to a mixture of internal olefins. A more detailed study of this reaction has been carried out by Manuel (47) who



has shown that the monoolefins are isomerized to give the distribution of isomers which would be expected on the basis of their relative thermodynamic stabilities. Sternberg and co-workers have also shown that similar isomerizations of olefins occur in the presence of hydroiron carbonyl anions (48, 49). Two possible mechanisms for the isomerization of the monoolefins have been proposed (47); the essentials are outlined in Eqs. (1-2).

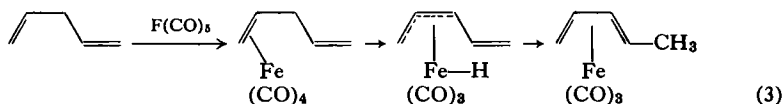


Allyl alcohol has been isomerized to propionaldehyde by reaction with $\text{Fe}(\text{CO})_5$ and a mechanism similar to that shown in Eq. (2) has been suggested (50).

Analogous intermediates could possibly be involved in the formation of conjugated diene complexes from nonconjugated dienes. Thus the formation of *trans*-1,3-pentadiene-iron tricarbonyl from 1,4-pentadiene could proceed by the route shown in Eq. (3).

Analogous intermediates can be written for the isomerization of conjugated dienes (41) and can explain the formation of the optically inactive α -terpinene complex from *d*-limonene.

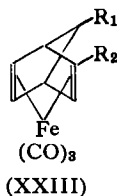
Another complication in the formation of acyclic diene-Fe(CO)₃ complexes is the formation of complexes derived from dimeric forms of the diene. This was first noted by Reihlen and co-workers (1), who obtained only complexes of formula (diene)₂-Fe(CO)₃ from the reactions of Fe(CO)₅ with isoprene and 2,3-dimethylbutadiene. It has been shown that butadiene and



isoprene give as by-products the same complexes as obtained from 4-vinylcyclohexene and dipentene (42). These products result no doubt from Diels-Alder-type dimerization of the diene followed by complex formation with rearrangement of the double bonds. The product of formula (C₆H₈)₂Fe(CO)₃ obtained from *trans*-1,3,5-hexatriene and Fe₃(CO)₁₂ possibly belongs to the same category (51). The formation of the dimeric complexes may be suppressed by using photochemical reactions (34).

2. Nonconjugated Diene-Iron Tricarbonyl Complexes

There are several well-authenticated cases recorded in which nonconjugated dienes react with iron carbonyls to give diene complexes without rearrangement, apart from the doubtful case of 1,5-cyclooctadiene (34, 44). Bicycloheptadiene was found to yield the complex (VIII) (52-54). Physical properties as well as degradation with liberation of bicycloheptadiene indicate that skeletal rearrangement has not occurred.



Derivatives of bicycloheptadiene that form diene-iron tricarbonyl complexes (XXIII) are listed in Table IV.

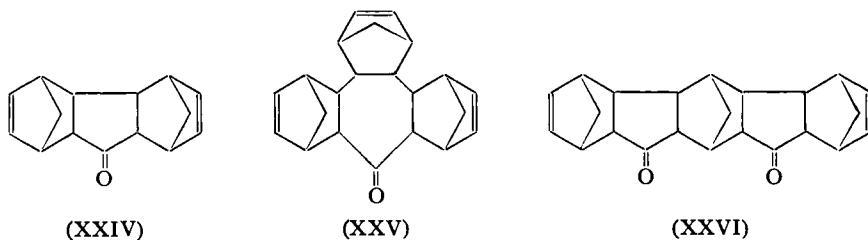
The reaction of bicycloheptadiene with Fe(CO)₅ has also produced a number of organic compounds of interest (56-58). As many as four dimers of bicycloheptadiene and five ketones may be obtained. The ketonic products appear to contain bicycloheptenyl units joined by carbonyl bridges. Representative formulae for these materials are given by (XXIV-XXVI).

TABLE IV
SUBSTITUTED BICYCLOHEPTADIENE COMPLEXES (XXIII)

Substituent		Reference
R ₁	R ₂	
H	H	(52, 53, 54)
H	CHO	(55)
H	CO ₂ C ₂ H ₅	(55)
H	CO ₂ H ^a	(55)
(CH ₃) ₃ CO—	H	(42)
CH ₃ CO ₂	H	(42)
OH	H ^a	(42)

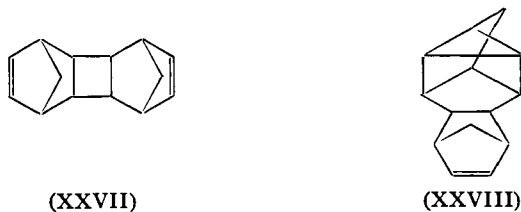
^a Obtained by hydrolysis of preceding esters.

The ketone (XXIV) was postulated to have *endo-trans-endo* configuration by Bird and co-workers (56). More recently however arguments stemming from NMR studies by Green and Lucken support an *exo-trans-exo* configuration (59). Bird and co-workers have also suggested structures (XXVII) and (XXVIII) for two of the dimers (58).

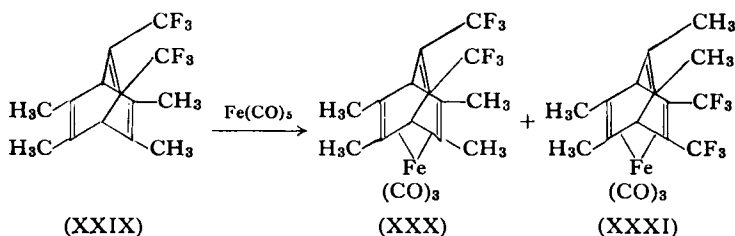


A cage structure has been proposed for a saturated dimer produced in the reaction (57, 58).

The 2,2,2-bicyclooctatriene derivative (XXIX) has also been found to give nonrearranged diene-iron complexes (60). Two products are obtained

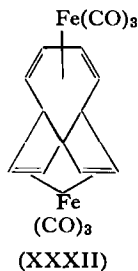


from the reaction of (XXIX) with $\text{Fe}(\text{CO})_5$. Structures (XXX) and (XXXI) are assigned to these on the basis of NMR studies, which indicate a symmetrical structure for the compound (XXX).



It is obvious that in these systems rearrangements similar to those noted are excluded because of the presence of bridging groups. Certain other dienes which do not have a 1,3 relationship of the double bonds, e.g., duroquinone, also exist as ligands in iron carbonyl complexes; these will be taken up in Section V.

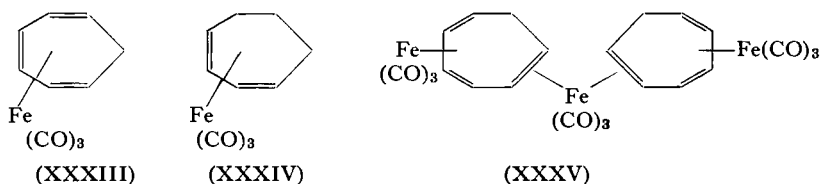
It seems possible that a binuclear complex containing two iron atoms bonded to a 1,3-diene and a nonconjugated diene, respectively, has been isolated. Cyclooctatetraene-iron tricarbonyl gives two Diels-Alder adducts with cyclooctatetraene. Each of these has the formula $\text{C}_{16}\text{H}_{16}\text{Fe}(\text{CO})_3$ and both, when heated with $\text{Fe}(\text{CO})_5$, eliminate benzene to form a $\text{C}_{10}\text{H}_{10}\text{Fe}_2(\text{CO})_6$ complex (61). From consideration of likely structures for the Diels-Alder adducts, it might be surmised that the product is (XXXII), although further investigation is necessary.



3. Triene-Iron Carbonyl Complexes

Several metal carbonyls are known to react with 1,3,5-cycloheptatriene to give metal complexes in which carbonyl groups have been displaced by three olefinic bonds and it seems possible that an analogous reaction might

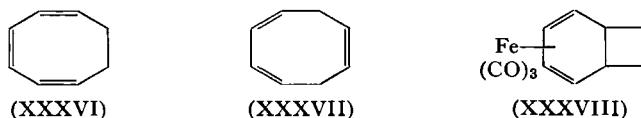
occur with $\text{Fe}(\text{CO})_5$. The formation of cycloheptatriene- $\text{Fe}(\text{CO})_2$ was in fact reported (52), but subsequent work has shown that the compound is cycloheptatriene- $\text{Fe}(\text{CO})_3$ (XXXIII) (27, 40). The complex displays an absorption in the infrared at 1660 cm^{-1} and can be reduced, under mild conditions, with hydrogen and Raney nickel, to cycloheptadiene- $\text{Fe}(\text{CO})_3$ (40). These properties indicate the presence of a noncomplexed olefinic bond in the molecule. The reaction of cycloheptatriene with $\text{Fe}(\text{CO})_5$, particularly for prolonged reaction periods, produces, in addition to (XXXIII), two other complexes. One of these compounds has been shown to be cycloheptadiene- $\text{Fe}(\text{CO})_3$ (XXXIV) and the other is a trinuclear complex for which the structure (XXXV) has been postulated.



The appearance of the complex (XXXIV) is interesting in that its formation must involve hydrogen transfer from the free diene or its complexed form. Although intramolecular hydrogen migration reactions are frequently encountered, such intermolecular hydrogen transfer reactions are most uncommon.

A binuclear complex, $\text{C}_9\text{H}_{10}[\text{Fe}(\text{CO})_3]_2$ is produced from $\text{Fe}(\text{CO})_5$ and vinylcycloheptatriene but this material has not been characterized (62).

An interesting reaction occurs in the case of the isomeric 1,3,5- and 1,3,6-cyclooctatrienes (XXXVI and XXXVII). Fischer and co-workers (63) reported that a mixture of these two hydrocarbons, when treated with iron carbonyl, gave rise to two complexes, one of formula $\text{C}_8\text{H}_{10}\text{Fe}(\text{CO})_3$ which was presumed to be the normal diene complex expected from (XXXVII).

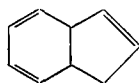


The other material analyzed as $\text{C}_8\text{H}_{10}\text{Fe}_2(\text{CO})_6$. The first of these complexes was independently prepared from a similar mixture of trienes by Manuel and Stone (19) who, observing that the material failed to absorb hydrogen or bromine, proposed the bicyclic structure (XXXVIII). These workers

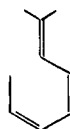
also showed that pure 1,3,5-cyclooctatriene was converted to (XXXVIII), together with a second isomeric complex which was unstable and could be converted to (XXXVIII) on further treatment with $\text{Fe}(\text{CO})_5$ (64). This second isomer may be the 1,3,5-cyclooctatriene- $\text{Fe}(\text{CO})_3$ complex. The bicyclic nature of the complex (XXXVIII) is supported by NMR data (40). Liberation of the organic ligand by treatment with triphenylphosphine gave bicyclooctadiene together with its valence tautomer (XXXVI).

The structure of the binuclear complex, $\text{C}_8\text{H}_{10}\text{Fe}_2(\text{CO})_6$, reported by Fischer and co-workers, remains unknown.

Another triene system which has been briefly studied is 8,9-dihydroindene (XXXIX) (65). With iron carbonyl this material affords an iron-tricarbonyl complex, the instability of which, it has been suggested, indicates two non-conjugated double bonds are involved in the bonding to Fe.



(XXXIX)



(XL)

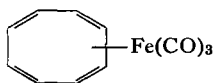
Only two instances of attempts to make acyclic triene-iron carbonyl complexes have been reported. Alloocimene (XL) forms an $\text{Fe}(\text{CO})_3$ complex when treated with $\text{Fe}_3(\text{CO})_{12}$ (34). In view of the possibility of rearrangement having occurred the structure of this material remains questionable.

trans-1,3,5-Hexatriene, besides affording the material $(\text{C}_6\text{H}_8)_2\text{Fe}(\text{CO})_3$ mentioned in Section III, A, 1, is also reported to form a complex of possible formula $\text{C}_6\text{H}_8\text{Fe}(\text{CO})_2$ when treated with $\text{Fe}_3(\text{CO})_{12}$ (51). If true this would be a very unusual system, but the material requires further investigation.

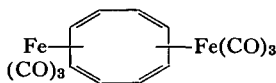
Substituted fulvenes react with iron carbonyls in an abnormal manner; these reactions are discussed in Section IV.

4. Cyclooctatetraene-Iron Tricarbonyl

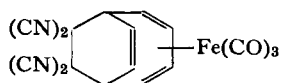
The preparation of cyclooctatetraene-iron tricarbonyl (XLI) was reported independently in 1959 by three separate research groups (18, 19, 20, 44, 66).



(XLI)



(XLII)



(XLIII)

The material is made from cyclooctatetraene and $\text{Fe}(\text{CO})_5$, reacting either thermally or photochemically. Two other products of formula $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$ (XLII) and $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_7$ also have been isolated from this reaction. The considerable interest shown in the compound (XLI) (13–21, 66–68) stemmed largely from the fact that it displayed only one proton resonance in the NMR studies, suggestive of a symmetrical structure having a planar ring for the C_8H_8 fragment. However, the X-ray studies, which were discussed in Section II, A, clearly indicated that this compound is best regarded as a diene- $\text{Fe}(\text{CO})_3$ complex.

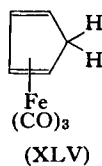
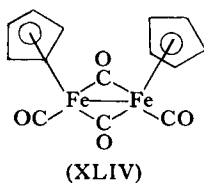
The reason why the material shows only one proton resonance is still not clear, nor is the fact that the complex resists hydrogenation and addition of bromine.

Compound (XLI) does not undergo a Diels-Alder reaction with maleic anhydride but recently a 1:1 adduct with tetracyanoethylene has been obtained (30, 61). Schrauzer and Eichler (61) have found that two isomeric products, presumed to be $\text{Fe}(\text{CO})_3$ complexes of cyclooctatetraene dimers, are obtained when (XLI) is irradiated in the presence of cyclooctatetraene. As mentioned in Section III, A, 2, these isomers, upon irradiation with $\text{Fe}(\text{CO})_5$, eliminate benzene to form the same binuclear complex $\text{C}_{10}\text{H}_{10}\text{Fe}_2(\text{CO})_6$. The structures of these complexes have not been rigorously established.

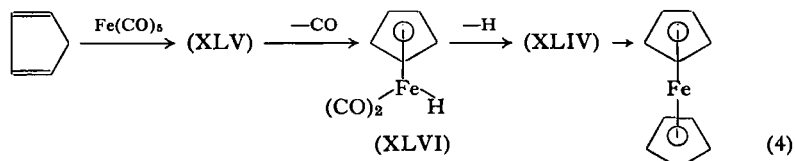
The structure of the binuclear complex (XLII) has already been discussed (Section II, A). The nature of the complex, $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_7$, has not been fully established, though, because it appears to contain bridging carbonyl groups, Manuel and Stone have suggested that it may be a derivative of $\text{Fe}_2(\text{CO})_9$ (18, 19).

5. Iron Carbonyl Derivatives of Cyclopentadiene

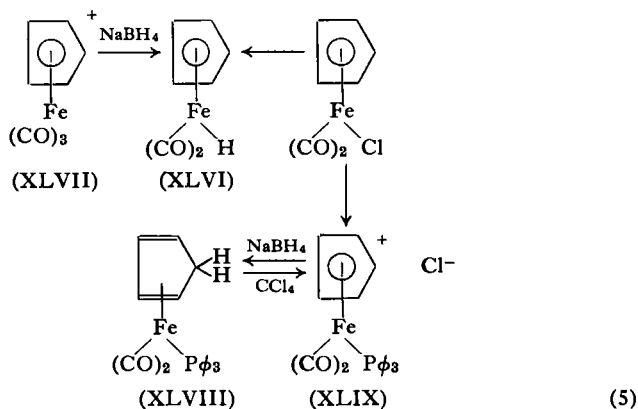
Cyclopentadiene and its derivatives react in an unusual manner with iron carbonyls. Reaction of cyclopentadiene with $\text{Fe}(\text{CO})_5$ under conditions normal for the preparation of diene-iron tricarbonyl complexes produces the binuclear complex (XLIV) and cyclopentene rather than (XLV) (69, 70).



The complex (XLIV) decomposes thermally to produce ferrocene and it has been postulated that both (XLV) and (XLIV) occur as intermediates in the synthesis of ferrocene from cyclopentadiene and $\text{Fe}(\text{CO})_5$ (21, 71). The reaction sequence of Eq. 4 is envisioned.



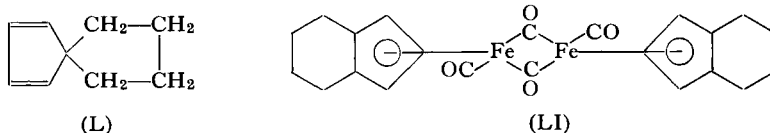
The spontaneous decomposition of (XLV) to (XLVI) has been suggested from separate studies (28). Reduction of the cation (XLVII) with NaBH_4 produces (XLVI) rather than (XLV); the compound (XLVI), in turn, readily decomposes at room temperature to produce (XLIV), with loss of hydrogen. It is interesting to note that whereas the iron tricarbonyl derivative of cyclopentadiene appears too unstable to allow isolation, the iron dicarbonyl-phosphine derivative (XLVIII) can be isolated by reduction of the corresponding cation (XLIX) (28). These reactions are outlined in Eq. 5.



The suggestion has been made that the greater stability of the dicarbonyl-triphenylphosphine complex (XLVIII) over that of the tricarbonyl complex (XLV) is due to the weaker back donation involved in the $\text{Fe}-\text{P}$ bond which in turn results in stronger bonding for the $\text{Fe}-\text{CO}$ ligands (28).

The great tendency for the cyclopentadiene- $\text{Fe}(\text{CO})_3$ complexes to rearrange to cyclopentadienyl-type complexes is impressively illustrated in

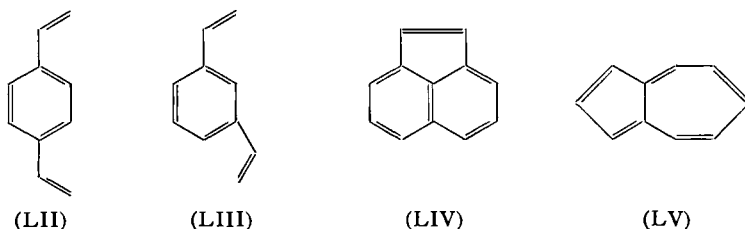
the reaction of the spiro compound (L) with $\text{Fe}(\text{CO})_5$. The product in this case is the compound (LI) and no diene- $\text{Fe}(\text{CO})_3$ complex was observed (72).



A comparable carbon skeletal rearrangement has never been reported for any other type of diene system.

6. Reactions with Aromatic Systems

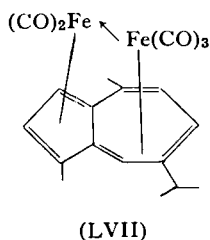
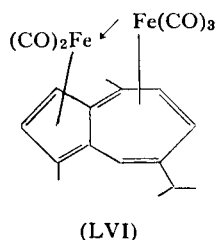
Benzene and its purely aromatic homologs (naphthalene, etc.) do not appear to react with iron carbonyls though iron carbonyl complexes can be obtained from several other aromatic systems. For example, the reaction of *m*- and *p*-divinylbenzenes (LII, LIII) with $\text{Fe}_3(\text{CO})_{12}$ leads to the formation of *m*- and *p*-divinylbenzene-diiron hexacarbonyl complexes (36). No analogous metal complexes were obtained from styrene or vinyltoluenes. The two divinyl complexes are stable crystalline solids and, as far as their structure is concerned, it has been suggested that in each case a vinylic bond and two pairs of π electrons from the benzene ring are used to bond to each of two $\text{Fe}(\text{CO})_3$ groups (36).



Acenaphthylene (LIV) also reacts with $\text{Fe}_3(\text{CO})_{12}$ to form a complex, $\text{C}_{12}\text{H}_8\text{Fe}_2(\text{CO})_6$ (65). The nature of the attachment of the iron atoms to the ring is not known.

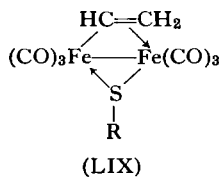
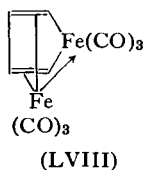
Azulene (LV), and several of its alkyl derivatives, give complexes of the form azulene $\cdot \text{Fe}_2(\text{CO})_5$ when treated with $\text{Fe}(\text{CO})_5$ (52, 73). In the case of guaiazulene (1,4-dimethyl-7-isopropylazulene) two isomeric complexes of this type have been isolated. Evidence for a similar isomeric pair has been found for 4-methylazulene (73). Once again the structure of these interesting complexes is not known with certainty. Physical data indicates that the two

iron atoms are attached on the same side of the plane of the azulene molecule, one to each ring. The suggestion is made (73) that the bonding of the Fe atoms to the ring involves bond fixation of the double bonds in the ring. Such a bond fixation could also account for the existence of the isomeric pairs found for the unsymmetrically substituted azulenes; possible formulas of the isomers obtained with guaiazulene would be (LVI) and (LVII).



7. Heterocyclic Aromatic Compounds

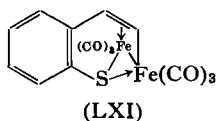
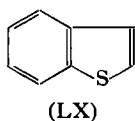
Thiophene has been reported to react with $\text{Fe}(\text{CO})_5$ to produce a material described as thiophene-iron dicarbonyl (52). However, a complex having very similar properties to this substance and also obtained from the reaction of thiophene and $\text{Fe}(\text{CO})_5$ or $\text{Fe}_3(\text{CO})_{12}$ was found not to contain sulfur (74) and the existence of thiophene-iron dicarbonyl is questionable. The material which does not contain sulfur is found to be identical to one of the products obtained upon reaction of acetylene with iron carbonyl, for which the binuclear structure (LVIII) has been proposed (38, 54, 75).



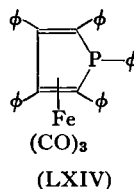
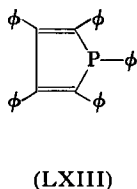
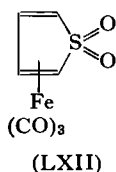
In this connection it is interesting that divinyl sulfide and other vinyl sulfides of the type $\text{R}-\text{S}-\text{CH}=\text{CH}_2$ react with $\text{Fe}_3(\text{CO})_{12}$ to form complexes of the composition $(\text{RSCCH}=\text{CH}_2) \cdot \text{Fe}_2\text{CO}_6$ for which the structural formula (LIX) has been advanced. Formation of such complexes necessitate the cleavage of a C—S bond and similar types of complexes may occur in the above desulfurization of thiophene (76).

With benzthiophene (LX), the reaction leads to the formation of a complex which contains both iron and sulfur. A binuclear complex similar in struc-

ture to the azulene complexes (Section III, A, 6) was proposed for this compound, but more recently it has been reformulated as structure (LXI) (74, 76).



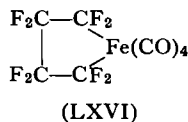
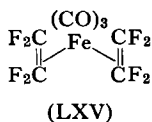
With thiophene sulfones, normal diene complexes can be obtained. Thus thiophene sulfones react to produce compounds of type (LXII) (77).



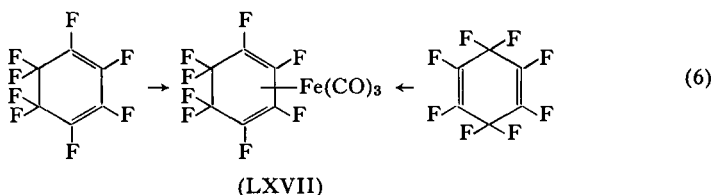
Pentaphenylphosphole (LXIII) reacts with $\text{Fe}_3(\text{CO})_{12}$ to give the complex (LXIV) and an analogous compound is also formed from the P-oxide derivatives of (LXIII) (78, 79). Molecular orbital calculations would suggest that (LXIV) is better regarded as a regular diene- $\text{Fe}(\text{CO})_3$ complex rather than a system involving an aromatic heterocyclic ring bonded to iron (80).

8. Fluorinated Olefins

Reactions of perfluoro olefinic compounds with iron carbonyls are also found to be somewhat unusual due undoubtedly to the high electronegativity of the fluorine atom. Tetrafluoroethylene was found to react with $\text{Fe}_3(\text{CO})_{12}$ to give a complex, first thought to be (LXV) (81) but subsequently shown to be the σ -bonded $\text{Fe}(\text{CO})_4$ complex (LXVI) (82, 83). The formation of (LXVI) in this manner is related to the fact that whereas Fe-alkyl bonds are very unstable, Fe-perfluoroalkyl bonds, as in the complex $(\text{CF}_3-\text{CF}_2)_2-\text{Fe}(\text{CO})_4$, are found to be quite stable (84).



What appear to be perfluorodiene- $\text{Fe}(\text{CO})_3$ complexes have been obtained from the reaction of perfluorodienes with iron carbonyls. Thus, as indicated in Eq. 6, the complex (LXVII) has been obtained from the reaction of either perfluoro-1,3-cyclohexadiene (81) or perfluoro-1,4-cyclohexadiene (85). The latter reaction involves a fluorine shift reminiscent of the hydrogen shift observed in the analogous reaction with 1,4-cyclohexadiene (43).



The reaction of perfluorobutadiene with $\text{Fe}_3(\text{CO})_{12}$ has yielded an organo-iron complex but its instability has deterred intensive investigation (85).

The electronic structures of the perfluorinated diene complexes are no more clear than those of the corresponding hydrocarbon complexes, but it is thought that σ bonding might be preferred over π bonding in these systems. Thus structure (LXVIIIa) is favored over (LXVIIIb) for the complex derived from hexafluorobut-2-yne and $\text{Fe}(\text{CO})_5$ (86) and the same might also be said of compound (LXVII).



B. Chemical Properties of Diene-Iron Tricarbonyl Complexes

1. Displacement Reactions of the Ligands

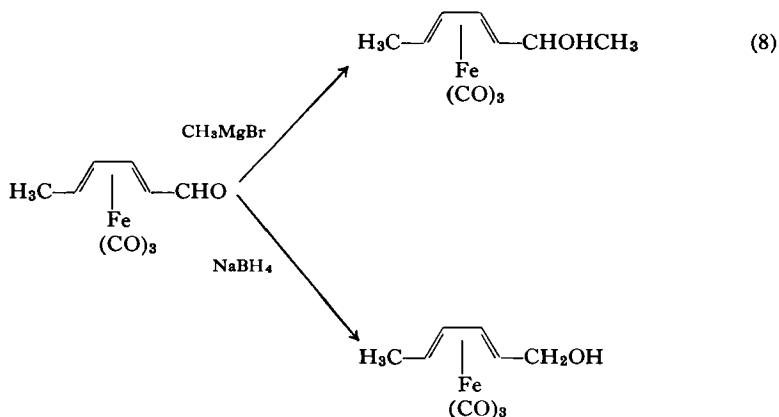
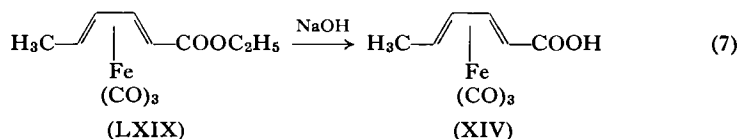
Reactions of diene- $\text{Fe}(\text{CO})_3$ complexes with other molecules capable of forming ligands with metals in low oxidation states can result in either displacement of the diene ligand or of one of the carbonyl groups. For example, the $\text{Fe}(\text{CO})_3$ complexes of *trans*-1,3-pentadiene (XXI) and bicyclooctadiene (XXXVIII) decompose when treated with triphenylphosphine with liberation of the hydrocarbon ligands (34, 19). Cyclooctatetraene-iron tricarbonyl gives cyclooctatetraene when treated with $\text{P}\phi_3$ but with $\text{As}\phi_3$ or $\text{Sb}\phi_3$ the

complexes of formula $C_8H_8Fe(CO)_2As\phi_3$ and $C_8H_8Fe(CO)_2Sb\phi_3$, respectively can be isolated (19).

Butadiene-iron tricarbonyl reacts with various esters of phenylphosphinous acid to give displacement of one carbonyl group and formation of complexes of the type $C_4H_6Fe(CO)_2 \cdot P\phi(OR)_2$ (87).

2. Chemical Reactions of the Dienes

Little data is available pertaining to chemical reactions of the diene moiety in which the diene unit is not involved. Several instances of hydrogenation or Diels-Alder reaction being performed on "free" double bonds in the ligand, have been discussed already. Reactions of other functional groups can also be conducted in the usual manner. Thus, as shown in Eq. 7, the acid complex (XIV), which cannot be made directly from sorbic acid (34), is readily obtained by hydrolysis of the ester (LXIX) which, in turn, can be made from ethyl sorbate and $Fe(CO)_5$ (32). Likewise, as shown in Eq. 8, an aldehyde function reacts normally with Grignard reagents and with $NaBH_4$ (32).



Oxidative reactions pose a difficulty in view of the ready collapse of the $Fe(CO)_3$ group under such conditions. Treatment of the complexes with such ions as Fe^{3+} or Ce^{4+} causes ready decomposition with liberation of the ligands.

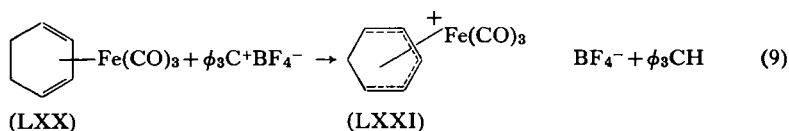
IV

RELATED IRON CARBONYL COMPLEXES

A. Dienyl-Iron Tricarbonyls

1. Cyclic Systems

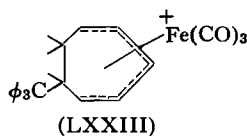
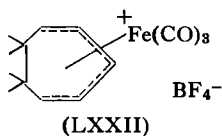
In 1958 Dauben and Honnen prepared the fluoroborate salt of cycloheptatrienyl-molybdenum tricarbonyl through reaction of cycloheptatriene-molybdenum tricarbonyl with triphenylmethyl fluoroborate (88). Fischer and Fischer (89) have shown that an analogous reaction between cyclohexadiene-iron tricarbonyl (LXX) and the triphenylmethyl cation leads to the formation of a salt of the cyclohexadienyliron tricarbonyl cation (LXXI), Eq. 9. In the cation (LXXI), and in the analogous complexes described below, it is assumed that there are five sp^2 -type carbon atoms simultaneously bonded to the iron atom.



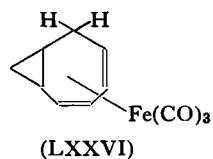
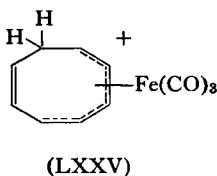
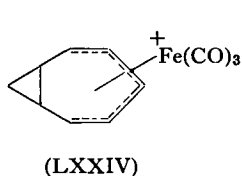
The direction of the reaction shown in Eq. 9 indicates that the cation (LXXI), which might formally be regarded as a carbonium ion complexed to Fe(CO)_3 , is more stable than the triphenylmethyl cation. The opposite is true when comparing the relative stabilities of the noncomplexed cyclohexadienyl cation and the triphenylmethyl cation. Viewed in this way the decreased electrophilicity of the cation (LXXI) may be ascribed to the large extent of electron transfer from the metal to the ligand via back donation. In line with this is the fact that cationic complexes of this type show abnormally high carbonyl absorption frequencies in the infrared.

Recent work by several groups has shown that the dienyl- Fe(CO)_3 unit exists as a stable group present in several related cationic species. Thus Dauben and Bertelli (27) have prepared cycloheptadienyl-iron tricarbonyl fluoroborate (LXXII) from cycloheptadiene- Fe(CO)_3 (XXXIV) and triphenylmethyl fluoroborate. The inherent stability of the dienyl- Fe(CO)_3 grouping is again seen in the reaction of cycloheptatriene-iron tricarbonyl (XXXIII) with the triphenylmethyl cation. Hydride abstraction to give the cycloheptatrienyl- Fe(CO)_3 cation does not occur but rather the triphenylmethyl cation adds to the free olefinic bond to produce the cation (LXXIII)

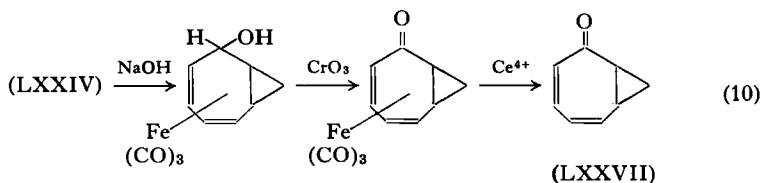
(27). In a related reaction cycloheptatriene-Fe(CO)₃ reacts with HBF₄, and other strong acids, to give, by proton addition to the free double bond, salts of the cation (LXXII) (27, 40, 90).



Cyclooctatetraene-Fe(CO)₃ also is found to add strong acids to produce salts of dienyl-Fe(CO)₃ cations (91, 92); recent work (30, 31) has shown that the cation formed in these reactions has the bicyclic structure (LXXIV) rather than the structure (LXXV), which would be expected from simple proton addition. Salts of the cation (LXXIV) lose a proton when treated



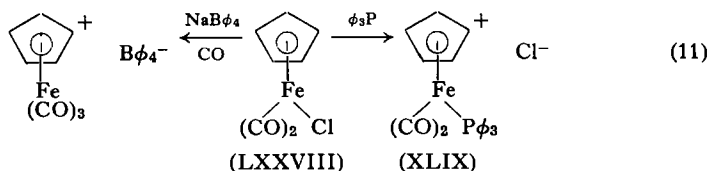
with water, regenerating cyclooctatetraene-Fe(CO)₃ (91); with NaBH₄ they produce the bicyclo[5.1.0]octadiene-Fe(CO)₃ complex (LXXVI) (30, 31). By means of the reactions indicated in Eq. 10 the cation (LXXIV) has proved to be useful for the synthesis of homotropone (LXXVII) (93).



2. Cyclopentadienyliron Carbonyl Compounds

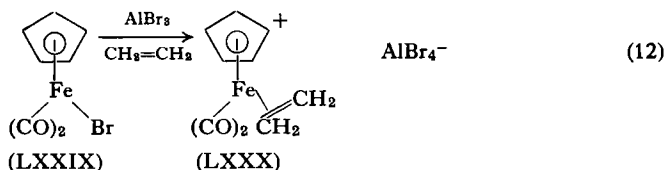
Salts of the cyclopentadienyliron tricarbonyl cation (XLVII) have been reported independently by Wilkinson and co-workers (28) and by Fischer and Fichtel (94). The former group found that cyclopentadienylchloroiron dicarbonyl (LXXVIII) [obtained from (XLIV) and HCl in air] reacted with sodium tetraphenylborate under pressure of carbon monoxide to give the tetraphenylborate salt of (XLVII). The covalent chloride (LXXVIII) gave

ionic chlorides of cations analogous to (XLVII), viz. (XLIX), when treated with triphenylphosphine. These reactions are shown in Eq. 11.



Reduction of the cation (XLVII) and the cation in (XLIX) with sodium borohydride was discussed in Section III, A, 5.

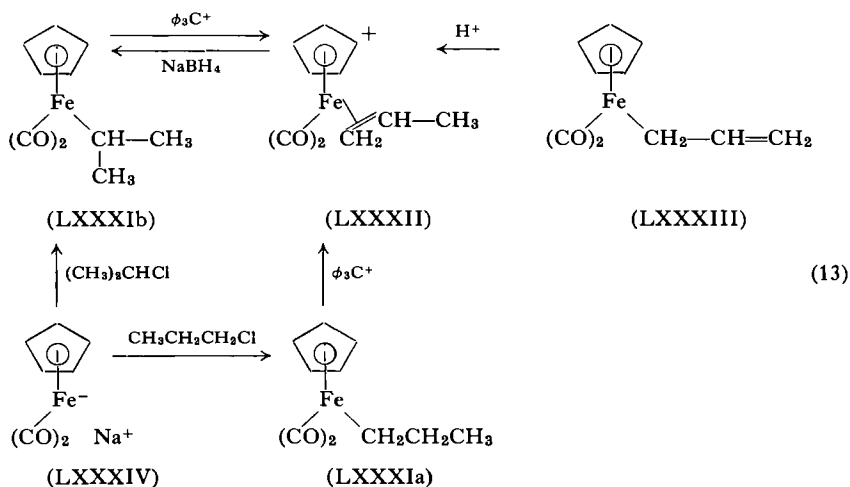
The iodo compound analogous to (LXXVIII) has been converted to the hexafluorophosphate salt of (XLVII) by reaction with HPF_6 and carbon monoxide (95).



Fischer and Fichtel (94) prepared the cation (XLVII) from the bromo compound (LXXIX) and AlBr_3 under pressure of carbon monoxide. The cation has also been prepared by treatment of the corresponding iodo compound with HPF_6 and carbon monoxide (95).

The incorporation of carbon monoxide in these reactions maintains the inert gas configuration of the iron atom in (XLVII) and thus promotes the ionization of the halogen. It is interesting that simple olefins may also serve in this capacity. Thus Fischer and Fichtel (94, 96) have obtained salts of the cyclopentadienyl- π -ethylene-iron dicarbonyl cation (LXXX) using ethylene in place of carbon monoxide (Eq. 12). Several olefins and other Lewis acids are found to undergo similar reactions.

An amusing interplay of σ - and π -bonded complexes involving similar cationic complexes has been shown to exist (Eq. 13) by Green and Nagy (97-100). A hydride ion may be abstracted from the σ -bonded *n*-propyl and isopropyl complexes (LXXXIa and b) produced from the dicarbonyl anion (LXXXIV) to generate the π -olefin complex (LXXXII). This cation reacts with NaBH_4 to give only the isopropyl complex back. In addition the σ -allyl complex (LXXXIII) can be protonated to form the same π -olefin cation (LXXXII).



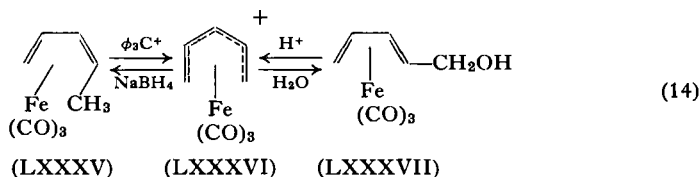
3. Acyclic Systems

In the pentadienyl cationic complexes described so far the five sp^2 hybridized carbon atoms are necessarily held in a *cis* configuration. This restriction of configuration does not hold in the case of acyclic pentadienyl systems. Nevertheless in each of the acyclic pentadienyl-Fe(CO)₃ cations so far prepared the arrangement of carbon atoms is *cis*. Reactions which might be expected to yield the *trans* configuration either fail to produce a stable cationic system or proceed to yield the *cis* isomer.

Thus *trans*-1,3-pentadiene-Fe(CO)₃ fails to react with the triphenylmethyl fluoroborate under conditions favorable for hydride abstraction in the cyclic series. On the other hand *cis*-1,3-pentadiene-iron tricarbonyl (LXXXV) reacts readily under the identical conditions to yield pentadienyl-iron tricarbonyl fluoroborate (LXXXVI) (32). The same cation is obtained from *trans*-2,4-pentadien-1-ol (LXXXVII) upon reaction with strong acids (37). Hydrolysis of the cation (LXXXVI) regenerates the *trans*-alcohol complex while reduction with NaBH₄ produces (LXXXV); this latter reaction constitutes the only means to date of making the *cis*-pentadiene complex (32). These reactions are given in Eq. 14.

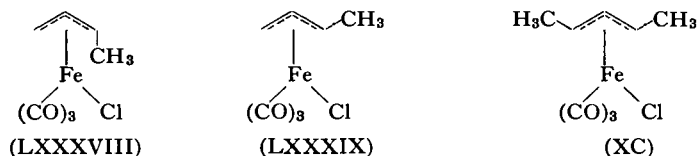
The 1-methyl and 1,5-dimethyl derivatives of (LXXXVI) have been prepared from the corresponding hexadienol- and heptadienol-Fe(CO)₃ complexes. The same type of geometrical inversions occur upon formation of the cations and are also seen in their reactions with water (32, 37).

Reaction of the 1-methyl derivative of (LXXXVI) with metallic zinc produces the bis(iron tricarbonyl) derivative of *trans-trans*-5,6-dimethyl-1,3,7,9-decatetraene. This reaction, which presumably proceeds via a pentadienyl-Fe(CO)₃ free radical intermediate, also involves geometrical inversion (32, 25). The cyclic cation (LXXI) reacts with zinc to give a dimeric product in which geometrical inversion cannot have occurred (42).



B. π -Allyliron Carbonyls

Ihrman and Impastato in 1961 reported that butadiene-Fe(CO)₃ reacted with hydrogen chloride to give a covalent addition product formulated as *anti*-1-methyl- π -allylchloroiron tricarbonyl (LXXXVIII) (101). Murdoch

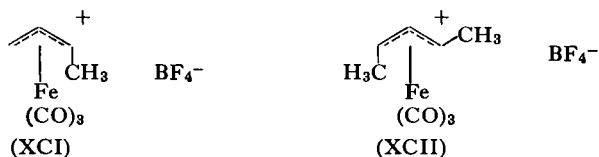


and Weiss later obtained the same product from reaction of *trans*-crotyl chloride with Fe₂(CO)₉ (102). NMR studies indicate however that the material is the *syn* isomer (LXXXIX) (103). The preparation of the *syn-syn*-dimethyl derivative (XC) from HCl and *trans*-1,3-pentadiene-Fe(CO)₃ confirms that the addition occurs with geometrical inversion (42).

The reaction of allyl halides with Fe₂(CO)₉ is a general one; in this way the parent π -allylhaloiron tricarbonyl and several of their derivatives have been prepared (102). Allyl iodides, but not chlorides or bromides, react with Fe(CO)₅ to give π -allyliodoiron tricarbonyl complexes (104).

A series of π -allyl-Fe(CO)₃ cationic complexes has been obtained by treatment of diene-Fe(CO)₃ complexes with strong acids such as HBF₄ or HClO₄ (50). These complexes are unusual in that the Fe atom is two electrons short of having the next inert gas configuration. Thus reaction of butadiene-Fe(CO)₃ with HBF₄ produces *anti*-1-methyl- π -allyliron tricarbonyl fluoroborate (XCI) while protonation of *trans*-1,3-pentadiene-

$\text{Fe}(\text{CO})_3$ gives the *syn-anti*-1,3-dimethyl- π -allyl- $\text{Fe}(\text{CO})_3$ salt (XCII). The nonequivalence of the methyl groups in the reaction indicates that geometrical inversion does not occur upon protonation.

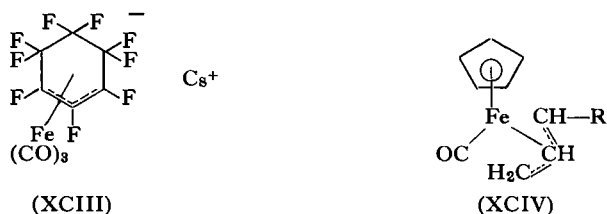


Similar salts can be prepared by the reaction of the covalent halides of type (LXXXIX) with AgBF_4 or AgClO_4 ; the configuration existing in the π -allyl group of the covalent halide is retained (42).

Reaction of these salts with water produces ketones and a mechanism of hydrogen migration, similar to that discussed earlier, has been proposed.

There is one reported instance of an anionic π -allyl- $\text{Fe}(\text{CO})_3$ complex (105). Perfluorocyclohexadiene- $\text{Fe}(\text{CO})_3$ (LXVII), when treated with cesium fluoride, gives rise to the cesium salt of the π -perfluorocyclohexenyl- $\text{Fe}(\text{CO})_3$ anion (XCIII).

Green and Nagy (100) have recently obtained π -cyclopentadienyl- π -allyliron monocarbonyl complexes (XCIV) by photolysis of corresponding σ -allyliron dicarbonyl complexes of type (LXII).



An experiment designed to produce a π -cyclopropenyliron carbonyl complex led instead to a different type of organoiron complex (106).

C. Monoolefin-Iron Tetracarbonyl Complexes

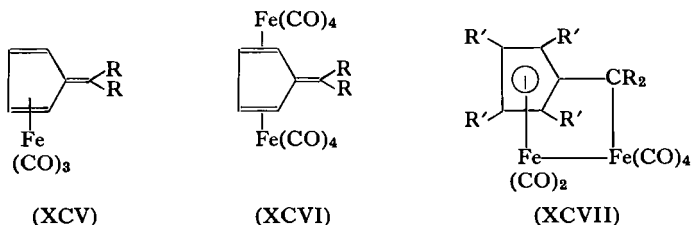
In the recent literature several instances have been reported of the formation of olefin-iron tetracarbonyl complexes. The first example was the preparation of acrylonitrile-iron tetracarbonyl from acrylonitrile and $\text{Fe}_2(\text{CO})_9$ (107). The X-ray data for this complex shows that the iron atom in this complex is bonded to the $\text{C}=\text{C}$ group rather than to the $\text{C}\equiv\text{N}$ or to the nitrogen atom (108, 109).

Butadiene- $\text{Fe}(\text{CO})_4$ and butadiene- $[\text{Fe}(\text{CO})_4]_2$ have been prepared from butadiene and $\text{Fe}_2(\text{CO})_9$ (110). In these complexes one of the carbon double bonds is π -bonded to the Fe atom. The butadiene- $\text{Fe}(\text{CO})_4$ complex reacts with HCl to form the 1-methyl- π -allylchloroiron tricarbonyl complex (LXXXIX), possibly through intermediate formation of a methyl- π -allyl- $\text{Fe}(\text{CO})_4$ cation (110).

Other olefin derivatives which form analogous complexes with $\text{Fe}_2(\text{CO})_9$, include maleic anhydride, maleic and fumaric acids and their esters, acrolein, and cinnamaldehyde (111). Several of these complexes have also been obtained upon irradiation of the olefinic compounds with $\text{Fe}(\text{CO})_5$ (112). Normal reactions of the functional groups of the ligand, e.g., esterification and hydrolysis, can be accomplished. Degradation of the maleic anhydride complex with HBr produces succinic acid (112).

D. Iron Carbonyl Complexes from Fulvenes

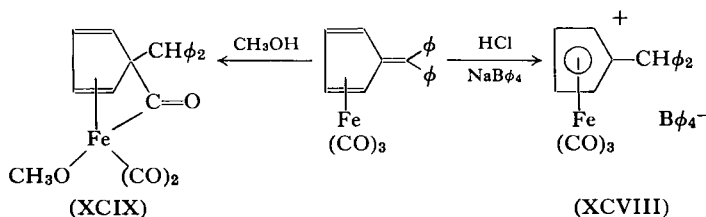
The reactions of fulvenes with iron carbonyls have been studied by Weiss and Hübel (113, 114). Upon reaction with $\text{Fe}(\text{CO})_5$, cyclopentadienyl iron compounds of type (XLIV) are obtained, but under the mild conditions possible with the use of $\text{Fe}_2(\text{CO})_9$, a variety of products, some of unknown structure, are obtained. The ω,ω -diaryl-substituted fulvenes may be caused to yield complexes of type (XCV) or (XCVI) depending on the duration of the reaction. In contrast, alkyl-substituted fulvenes give products for which the general structure (XCVII) has been proposed; the parent complex is obtained from reaction of acetylene with iron carbonyls (75, 115).



In addition to complexes of these types an ω,ω -diphenylfulvene- $\text{Fe}_2(\text{CO})_5$ complex has been obtained and some $\text{Fe}(\text{CO})_2$ and $\text{Fe}_2(\text{CO})_5$ complexes of the dimeric forms of the fulvenes have been isolated. The structure of these complexes has not been established.

The diene- $\text{Fe}(\text{CO})_3$ complex (XCV, R = phenyl) may be protonated to give a substituted cyclopentadienyliron tricarbonyl cation (XCVIII); with

methanol it forms an acyliron complex (XCIX). Other reactions of these compounds indicate a great tendency to form cyclopentadienyliron complexes.



V

IRON CARBONYL COMPLEXES DERIVED FROM ACETYLENES

A. Introduction

As part of a comprehensive study of carbonylation reactions Reppe and Vetter (2) reported in 1953 that reaction of acetylene with $\text{Fe}(\text{CO})_5$ produced, along with ethyl acrylate and hydroquinone, a stable organoiron compound $\text{FeC}_{11}\text{H}_7\text{O}_5$ (C). The compound (C), upon hydrolysis, gave hydroquinone and a new complex $\text{FeC}_7\text{H}_4\text{O}_3$ (CI) which, in turn, could be oxidized to $\text{FeC}_8\text{H}_4\text{O}_4$ (CII). A different complex, $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ (CIII), was obtained from the reaction of acetylene with $\text{H}_2\text{Fe}(\text{CO})_4$ in aqueous alkaline solution.

No structures were then postulated for these complexes but it was readily apparent that a novel area of organometallic chemistry had emerged. It is not surprising that the past decade has seen intense activity in this field.

Subsequent developments in this area have produced a large number of new organoiron complexes; the greater majority of these are found to be olefin-iron carbonyl complexes, hence their inclusion in this review.

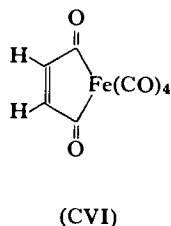
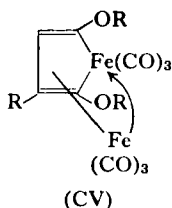
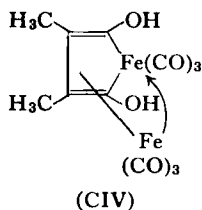
The subject does not lend itself to simple classification; we have found it convenient to divide the study into three sections, according to the different modes of synthesis of the various complexes.

B. Complexes from Iron Carbonyl Anions

The reaction of acetylene with $\text{NaHFe}(\text{CO})_4$, to give Reppe's complex (CIII), was studied by several groups (116, 117, 10). The complex was found to contain two acidic hydroxyl groups (117) and a contiguous chain of four carbon atoms (10). Analogous complexes were formed from other acetylenes

such as propyne and 2-butyne. Several possible structures for this type of complex were advanced (116, 117, 10, 5) but not until the X-ray data became available was the problem resolved.

Hock and Mills, in 1958, established that the best representation of the complex obtained from 2-butyne was as shown in formula (CIV) (6, 118). One iron atom and two of its three carbonyl ligands are very nearly coplanar with the four-carbon chain and its two methyl substituents. The other iron atom is approximately equidistant from the four ring carbon atoms and is apparently analogous to that in the butadiene- $\text{Fe}(\text{CO})_3$ complexes. An Fe—Fe bond, which would preserve the inert gas structure of the ring Fe atom, is assumed, the distance being 2.49 Å. The molecular orbital structure of this system has been discussed (119).



Case and co-workers (120) have demonstrated an interesting intramolecular exchange of the roles of the dissimilar σ - and π -bonded $\text{Fe}(\text{CO})_3$ groups. These authors isolated optically active forms of the unsymmetrical complexes of type (CV). The optically active complexes underwent rapid thermal racemization, particularly in the case of the anion derived from (CV, $\text{R} = \text{C}_2\text{H}_5$, $\text{R}' = \text{R}'' = \text{H}$), which would indicate a facile interchange of the two $\text{Fe}(\text{CO})_3$ groups without disruption of the complex.

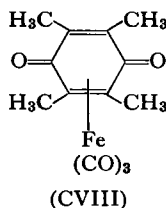
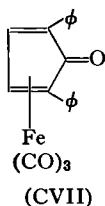
The complexes derived from several acetylenes have been oxidized with ferric chloride to produce, upon loss of an iron carbonyl residue, the corresponding derivatives of (CVI) (121).

The mechanism of the formation of complexes of type (CIV) is obscure; it has been suggested that $\text{Fe}_2(\text{CO})_8^{2-}$ rather than HFeCO_4^- is the active species in the reaction (122).

C. Complexes from Substituted Acetylenes and Iron Carbonyls

In the presence of $\text{Ni}(\text{CO})_4$, phenylacetylene was found (123) to react with $\text{Fe}(\text{CO})_5$ to produce a complex, at first thought to be an iron carbonyl-

bis(phenylacetylide) derivative. This material has subsequently been shown to be 2,5-diphenylcyclopentadienone- $\text{Fe}(\text{CO})_3$ (CVII) (124, 9, 125). Another early-known reaction illustrating the formation of unsaturated ketonic complexes is the formation of duroquinone- $\text{Fe}(\text{CO})_3$ (CVIII) from $\text{Fe}(\text{CO})_5$ and 2-butyne in sunlight (5). 1-Pentyne and 3-hexyne produce similar quinone derivatives. 2,3,4,5-Tetraphenylcyclopentadienone- $\text{Fe}(\text{CO})_3$ has been obtained from diphenylacetylene and $\text{Fe}_3(\text{CO})_{12}$ by Schrauzer (7, 39).



In 1959 Hübel and co-workers (8, 126) reported the results of a systematic study of the reactions of iron carbonyls with substituted acetylenes. Depending on the nature of the acetylene, the carbonyl employed, and the time and temperature of the reaction, many products of different types can be obtained. The range of synthesis is shown in Table V. The structures of many, though not all, of these complexes appear to have been established. The skeletal structures of these are as shown below.

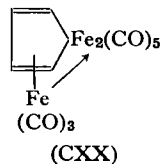
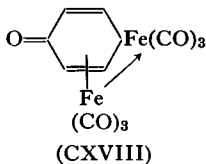
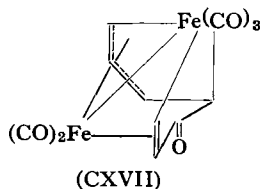
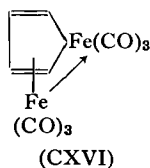
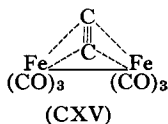
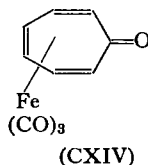
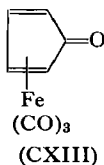
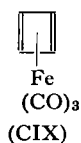


TABLE V
COMPLEXES DERIVED FROM SUBSTITUTED ACETYLENES

Number of iron atoms	Number of incorporated acetylene molecules (A = substituted acetylene) ^{a, b}				
	1	2	3	4	5
1	—	A ₂ Fe(CO) ₃ (CIX) 1, 2	A ₃ Fe(CO) ₂ (CX) 3	A ₄ Fe(CO) ₃ (CXI) 7	A ₅ Fe(CO) ₄ (CXII) 7, 8
1	—	A ₂ Fe(CO) ₄ (CXIII) 1, 2, 5, 6, 7 8, 9, 10	A ₃ Fe(CO) ₄ (CXIV) 7, 7', 8	—	—
2	AFe(CO) ₆ (CXV) 1, 2	A ₂ Fe ₂ (CO) ₆ (CXVI) 1, 2, 3, 4, 5, 6, 7, 8	A ₃ Fe ₂ (CO) ₆ (CXVII) 5, 7, 8	—	—
2	—	A ₂ Fe ₂ (CO) ₇ (CXVIII) 1, 2, 4, 5, 6	—	—	—
3	AFe ₃ (CO) ₁₀ (CXIX) 5	A ₂ Fe ₃ (CO) ₈ (CXX) 1, 1', 2, 5, 6	—	—	—

^a In the table the acetylenes (A) are numbered as follows:

1. Diphenylacetylene (7, 8, 38, 39, 126).
2. Di-*p*-chlorophenylacetylene (8, 38, 126).
3. Methylacetylene dicarboxylate (8, 38, 126).
4. 3-Hexyne (8, 38).
5. Methylphenylacetylene (8, 38).
6. Trimethylsilylphenylacetylene (8, 38).
7. Phenylacetylene (7, 8, 38, 124, 126).
8. *p*-Bromophenylacetylene (8, 38).
9. Trimethylsilylacetylene (8, 38).
10. Perfluoro-2-butyne (86).

^b The acetylenes di-trimethylsilylacetylene (38), di-*p*-nitrophenylacetylene (38), and acetylene dicarboxylic acid (38) do not form complexes.

The X-ray data (127) of (CIX.1) confirm the tetraphenylcyclobutadiene-Fe(CO)₃ structure proposed earlier (8, 16, 38). Reduction of the complex with LiAlH₄ or Na in liquid NH₃ produces tetraphenylbutadiene and tetraphenylbutane (8, 38).

Cyclopentadienone complexes of type (CXIII) have in many cases been

prepared from the reaction of the appropriate dienone with iron carbonyl (7, 38, 77). The formation of the cyclopentadienone derivatives appears to be stereospecific; in complexes (CXIII.5) and (CXII.7) the only isomers obtained have phenyl groups in the 2- and 5-positions of the ring (7, 77).

The monoacetylene complexes (CXV) are believed to contain bridging acetylenic units; reduction of (CXV.1) with Na and liquid NH_3 gives dibenzyl (38).

The complexes (CXVI) are analogous to the derivatives (CIV) discussed in Section V, B. The tetraphenyl derivative (CXVI.1) gives the tetracyclone- $\text{Fe}(\text{CO})_3$ complex (CXIII.1) upon bromination and with methanolic NaOH yields tetraphenylbutadiene- $\text{Fe}(\text{CO})_3$ (38, 39, 128). Reaction of this tetraphenyl derivative with appropriate reagents has provided a novel synthesis of furans, thiophenes, selenophenes, pyrroles, phospholes, and arsoles (38, 78, 128).

The complex (CXVIII.1), upon heating or photolysis, is converted to the cyclopentadienone complex (CXIII.1); various other reactions lead to the formation of tetraphenylquinone or hydroquinone (38, 39). Heterocyclic compounds such as pyrones and thiapyrones are obtained upon displacement of the ring $\text{Fe}(\text{CO})_3$ group (128).

The complex (CXX.1) may be converted to either (CXVI.1) or (CXIII.1) (38, 39). There exists evidence for the presence of bridging carbonyl groups in this complex (38, 39).

The structure of the triphenyltropone complex (CXVI.7), determined by Smith and Dahl (23), has been discussed in Section II, A.

The unusual bicyclic structure containing a π -allyl linkage proposed for (CXVII.7) is based upon X-ray data obtained by King (129). Thermal decomposition gives either 1,3,5-triphenylbenzene or 2,4,6-triphenyltropone- $\text{Fe}(\text{CO})_3$ complexes (CXIV.7) and (CXIV.7').

The structures of the remaining types of compounds listed in Table V have not been established; complexes of type (CXI) and (CXII) contain ketonic carbonyl groups (38).

The possible molecular orbital structure for many of these complexes has been discussed (16, 24, 80, 119, 130, 131).

D. Complexes from Acetylene and Iron Carbonyls

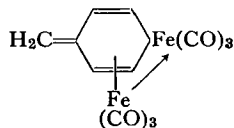
The complexes first isolated by Reppe from acetylene and $\text{Fe}(\text{CO})_5$, $\text{FeC}_{11}\text{H}_7\text{O}_5$ (C), $\text{FeC}_8\text{H}_4\text{O}_4$ (CI), and $\text{FeC}_7\text{H}_4\text{O}_3$ (CII), were reinvestigated in 1960 by Wilkinson (54) and by Weiss (132) and their co-workers.

The complex (CI) was found to be cyclopentadienone- $\text{Fe}(\text{CO})_3$, while (CII) is postulated to be cyclopentadienone- $\text{Fe}(\text{CO})_2$ (54) or the dimer thereof (132); cryoscopic and ebullioscopic molecular weight determinations vary considerably in different solvents (54, 132, 133). Both (CI) and (CII) give cyclopentadienone-triposphine iron dicarbonyl when treated with triphenylphosphine; the two are interconvertible by oxidation and carbonylation reactions (133).

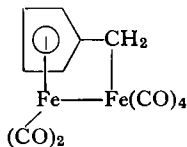
It was shown by direct synthesis that the complex (C) was merely a molecular complex of two molecules of (CI) and one of hydroquinone; the lower molecular weight originally supposed was found to be due to dissociation. The compound (CI) is unusually basic and forms adducts with acids such as phenols, FeCl_3 , and the halogen acids (132, 133).

As with the substituted acetylenes, the reactions of acetylene itself with $\text{Fe}_3(\text{CO})_{12}$ or $\text{Fe}_2(\text{CO})_9$ leads to the isolation of more complex products than with $\text{Fe}(\text{CO})_5$. Hübel and co-workers have, to date, isolated twelve complexes from the two reactions (75, 115). In addition to the three complexes isolated first by Reppe there is formed the binuclear complex (LVIII), also obtained from thiophene, which is analogous to type (CXVI) complexes obtained from substituted acetylenes. A tropone- $\text{Fe}(\text{CO})_3$ complex (CXXI) is also obtained. Another known product isolated is the complex (CVI) which was also obtained by oxidation of Reppe's acidic complex (CIII) as discussed in Section V, B.

Two other products which are unlike those obtained in previous reactions are the binuclear complexes (CXXII) and (CXXIII). The formation of these complexes must involve hydrogen migration. Compound (CXXIII) is



(CXXII)



(CXXIII)

analogous to products derived from certain substituted fulvenes (Section IV, D). Besides these complexes there are four other products having molecular formulas $(\text{C}_2\text{H}_2)_5\text{Fe}_2(\text{CO})_6$, $(\text{C}_2\text{H}_2)_2\text{-Fe}_3(\text{CO})_8$, $(\text{C}_2\text{H}_2)_3\text{Fe}_2(\text{CO})_7$, and $(\text{C}_2\text{H}_2)_4\text{Fe}(\text{CO})_3$, to which complete structures have not been assigned.

The chemistry of the tropone- $\text{Fe}(\text{CO})_3$ complex (CXXI) has been studied by Weiss and Hübel (134). Like the corresponding cyclopentadienone complex, it also forms adducts with hydroquinone, but, unlike the former

compound, it gives normal ketone derivatives. Catalytic reduction with H_2 and platinum produces a mixture of 2,4-cycloheptadienone and 3,5-cycloheptadienone- $Fe(CO)_3$ complexes; reduction with zinc and acetic acid gives dimeric complex products.

ACKNOWLEDGMENT

We thank Professor L. F. Dahl for kindly providing us with Fig. 4 of the text.

REFERENCES

1. H. Reihlen, A. Gruhl, G. von Hessling, and O. Pfengle, *Ann. Chem.* **482**, 161 (1930).
2. W. Reppe and H. Vetter, *Ann. Chem.* **582**, 133 (1953).
3. P. L. Veltman, U.S. patent 2,409,167 (1946).
4. B. F. Hallam and P. L. Pauson, *J. Chem. Soc.* p. 642 (1958).
5. H. W. Sternberg, R. Markby, and I. Wender, *J. Am. Chem. Soc.* **80**, 1009 (1958).
6. A. A. Hock and O. S. Mills, *Proc. Chem. Soc.* p. 233 (1958).
7. G. N. Schrauzer, *Chem. Ind. (London)* p. 1403 (1958).
8. W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Krüerke, D. A. Brown, G. D. S. King, and C. Hoogzand, *J. Inorg. Nucl. Chem.* **9**, 204 (1959).
9. F. A. Cotton and J. R. Leto, *Chem. Ind. (London)* p. 1592 (1958).
10. R. Clarkson, E. R. H. Jones, P. C. Wailes, and M. C. Whiting, *J. Am. Chem. Soc.* **78**, 6206 (1956).
11. O. S. Mills and G. Robinson, *Proc. Chem. Soc.* p. 421 (1960).
12. M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 3753 (1959).
13. B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.* **83**, 4862 (1961).
14. B. Dickens and W. N. Lipscomb, *J. Chem. Phys.* **37**, 2084 (1962).
15. B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.* **83**, 489 (1961).
16. D. A. Brown, *J. Inorg. Nucl. Chem.* **10**, 39 (1959).
17. F. A. Cotton, *J. Chem. Soc.* p. 400 (1960).
18. T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.* p. 90 (1959).
19. T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 366 (1960).
20. A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan* **32**, 880 (1959).
21. P. L. Pauson, *Proc. Soc. Chem.* p. 297 (1960).
22. G. K. Wertheim and R. H. Herber, *J. Am. Chem. Soc.* **84**, 2274 (1962).
23. D. J. Smith and L. F. Dahl, *J. Am. Chem. Soc.* **84**, 1743 (1962).
24. D. A. Brown, *J. Inorg. Nucl. Chem.* **13**, 212 (1960).
- 24a. M. J. S. Dewar, "Hyperconjugation." Ronald Press, New York, 1962.
25. D. H. Gibson and R. Pettit, unpublished results.
26. J. D. Roberts and C. Green, *J. Am. Chem. Soc.* **68**, 214 (1946).
27. H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.* **83**, 497 (1961); H. J. Dauben, personal communication.
28. A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.* p. 3172 (1961).
29. K. Noack, *Helv. Chim. Acta* **45**, 1847 (1962).
30. A. Davison, W. McFarlane, and G. Wilkinson, *Chem. Ind. (London)* p. 820 (1962).
31. A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 4821 (1962).
32. J. E. Mahler and R. Pettit, unpublished results.

33. B. Nicholls and M. C. Whiting, *J. Chem. Soc.* p. 551 (1959).
34. R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.* **16**, 233 (1961).
35. M. Cais and M. Feldkimer, *Tetrahedron Letters* p. 444 (1961).
36. T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.* **83**, 3597 (1961).
37. J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.* **84**, 1511 (1962).
38. W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.* **10**, 250 (1959).
39. G. N. Schrauzer, *J. Am. Chem. Soc.* **81**, 5307 (1959).
40. R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 594 (1961).
41. R. Kochar and R. Pettit, unpublished results.
42. G. F. Emerson and R. Pettit, unpublished results.
43. J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.* **83**, 2955 (1961).
44. A. Nakamura and N. Hagihara, *Mem. Inst. Sci. Ind. Res. Osaka Univ.* **17**, 187 (1960).
45. T. A. Manuel and F. G. A. Stone, *Chem. Ind. (London)* p. 231 (1960).
46. F. Asinger and O. Berg, *Chem. Ber.* **88**, 445 (1955).
47. T. A. Manuel, *J. Org. Chem.* **27**, 3941 (1962).
48. H. W. Sternberg, R. Markby, and I. Wender, *J. Am. Chem. Soc.* **78**, 5704 (1956).
49. H. W. Sternberg, R. Markby, and I. Wender, *J. Am. Chem. Soc.* **79**, 6116 (1957).
50. G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.* **84**, 4591 (1962).
51. J. Xavier, M. Thiel, and E. R. Lippincott, *J. Am. Chem. Soc.* **83**, 2403 (1961).
52. R. Burton, M. L. H. Green, E. W. Abel, and G. Wilkinson, *Chem. Ind. (London)* p. 1592 (1958).
53. R. Pettit, *J. Am. Chem. Soc.* **81**, 1266 (1959).
54. M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 989 (1960).
55. R. Pettit, unpublished results.
56. C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind. (London)* p. 20 (1960).
57. D. M. Lemal and K. S. Shim, *Tetrahedron Letters* p. 368 (1961).
58. C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters* p. 373 (1961).
59. M. Green and E. A. C. Lucken, *Helv. Chim. Acta* **45**, 1870 (1962).
60. R. B. King, *J. Am. Chem. Soc.* **84**, 4705 (1962).
61. G. N. Schrauzer, and S. Eichler, *Angew. Chem.* **74**, 585 (1962).
62. R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.* **83**, 3590 (1960).
63. E. O. Fischer, C. Palm, and H. P. Fritz, *Chem. Ber.* **92**, 2645 (1959).
64. T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 6240 (1960).
65. R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 4557 (1960).
66. M. D. Rausch and G. N. Schrauzer, *Chem. Ind. (London)* p. 957 (1959).
67. H. P. Fritz and H. Keller, *Chem. Ber.* **95**, 158 (1962).
68. H. P. Fritz, *Chem. Ber.* **95**, 820 (1962).
69. T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.* **1**, 165 (1955).
70. B. F. Hallam, O. S. Mills, and P. L. Pauson, *J. Inorg. Nucl. Chem.* **1**, 313 (1955).
71. H. W. Sternberg and I. Wender, *Chem. Soc. (London) Spec. Publ.* **13**, 35 (1959).
72. B. F. Hallam and P. L. Pauson, *J. Chem. Soc.* p. 646 (1958).
73. R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 4290 (1960).
74. H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols, and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 4749 (1960).
75. W. Hübel and E. Weiss, *Chem. Ind. (London)* p. 703 (1959).
76. R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.* **83**, 3600 (1961).
77. E. Weiss and W. Hübel, *J. Inorg. Nucl. Chem.* **11**, 42 (1959).
78. E. H. Braye and W. Hübel, *Chem. Ind. (London)* p. 1250 (1959).

79. E. H. Braye, W. Hübel, and I. Caplier, *J. Am. Chem. Soc.* **83**, 4406 (1961).
80. D. A. Brown, *J. Chem. Soc.* p. 929 (1962).
81. K. F. Watterson and G. Wilkinson, *Chem. Ind. (London)* p. 991 (1959).
82. K. F. Watterson and G. Wilkinson, *Chem. Ind. (London)* p. 1358 (1960).
83. T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.* **83**, 249 (1961).
84. R. B. King, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.* p. 69 (1961).
85. H. H. Hoehn, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.* p. 2738 (1961).
86. J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.* p. 3488 (1962).
87. A. N. Nesmeyanov, K. N. Anisimov, and N. E. Kolonova, *Isv. Akad. Nauk SSSR Otd. Khim. Nauk* p. 722 (1962).
88. H. J. Dauben and L. R. Honnen, *J. Am. Chem. Soc.* **80**, 5570 (1958).
89. E. O. Fischer and R. D. Fischer, *Angew. Chem.* **72**, 919 (1960).
90. G. Winkhaus and G. Wilkinson, *Proc. Chem. Soc.* p. 311 (1958).
91. G. N. Schrauzer, *J. Am. Chem. Soc.* **83**, 2966 (1961).
92. A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *Chem. Ind. (London)* p. 553 (1961).
93. J. D. Holmes and R. Pettit, *J. Am. Chem. Soc.* **85**, 2531 (1963).
94. E. O. Fischer and K. Fichtel, *Chem. Ber.* **95**, 2063 (1962).
95. R. B. King, *Inorg. Chem.* **1**, 964 (1962).
96. E. O. Fischer and K. Fichtel, *Chem. Ber.* **94**, 1200 (1961).
97. M. L. H. Green and P. L. I. Nagy, *Proc. Chem. Soc.* p. 378 (1961).
98. M. L. H. Green and P. L. I. Nagy, *Proc. Chem. Soc.* p. 74 (1962).
99. M. L. H. Green and P. L. I. Nagy, *J. Am. Chem. Soc.* **84**, 1310 (1962).
100. M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.* p. 189 (1963).
101. F. J. Impastato and K. G. Ihrman, *J. Am. Chem. Soc.* **83**, 3726 (1961).
102. H. D. Murdoch and E. Weiss, *Helv. Chim. Acta* **45**, 1927 (1962).
103. J. E. Lancaster, personal communication quoted in ref. (102).
104. R. A. Plowman and F. G. A. Stone, *Z. Naturforsch.* **17b**, 575 (1962).
105. G. W. Parshall and G. Wilkinson, *J. Chem. Soc.* p. 1132 (1962).
106. C. E. Coffey, *J. Am. Chem. Soc.* **84**, 118 (1962).
107. S. F. A. Kettle and L. E. Orgel, *Chem. Ind. (London)* p. 49 (1960).
108. A. R. Luxmoore and M. R. Truter, *Proc. Soc. Chem.* p. 466 (1960).
109. A. R. Luxmoore and M. R. Truter, *Acta Cryst.* **15**, 1117 (1962).
110. H. D. Murdoch and E. Weiss, *Helv. Chim. Acta* **45**, 1156 (1962).
111. E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta* **46**, 288 (1963).
112. G. O. Schenck, E. Koerner von Gustorf, and Mon-Jon Jun, *Tetrahedron Letters* p. 1059 (1962).
113. E. Weiss and W. Hübel, *Angew. Chem.* **73**, 298 (1961).
114. E. Weiss and W. Hübel, *Chem. Ber.* **95**, 1186 (1962).
115. E. Weiss, R. Merenyi, and W. Hübel, *Chem. Ber.* **95**, 1155 (1962).
116. I. Wender, R. A. Friedel, R. Markby, and H. W. Sternberg, *J. Am. Chem. Soc.* **77**, 4946 (1955).
117. H. W. Sternberg, R. A. Friedel, R. Markby, and I. Wender, *J. Am. Chem. Soc.* **78**, 3621 (1956).
118. A. A. Hock and O. S. Mills, *Acta Cryst.* **14**, 139 (1961).
119. D. A. Brown, *J. Inorg. Nucl. Chem.* **11**, 9 (1959).
120. J. R. Case, E. R. H. Jones, N. V. Schwarz, and M. C. Whiting, *Proc. Chem. Soc.* p. 256 (1962).

121. J. R. Case, R. Clarkson, E. R. H. Jones, and M. C. Whiting, *Proc. Chem. Soc.* p. 150 (1959).
122. J. R. Case and M. C. Whiting, *J. Chem. Soc.* p. 4632 (1960).
123. E. R. H. Jones, P. C. Wailes, and M. C. Whiting, *J. Chem. Soc.* p. 4021 (1955).
124. G. N. Schrauzer, *Chem. Ind. (London)* p. 1404 (1958).
125. J. R. Leto and F. A. Cotton, *J. Am. Chem. Soc.* **81**, 2970 (1959).
126. W. Hübel, British patent 885,514 (1961).
127. R. P. Dodge and V. Schomaker, *Nature* **186**, 798 (1960).
128. E. H. Braye, C. Hoogzand, W. Hübel, U. Krüerke, R. Merenyi, and E. Weiss, *Advan. Chem. Coordination Compounds* p. 190 (1959).
129. G. D. S. King, *Acta Cryst.* **15**, 243 (1962).
130. D. A. Brown, *J. Inorg. Nucl. Chem.* **10**, 49 (1959).
131. E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.* **84**, 4633 (1962).
132. E. Weiss, R. Merenyi, and W. Hübel, *Chem. Ind. (London)* p. 407 (1960).
133. E. Weiss, R. Merenyi, and W. Hübel, *Chem. Ber.* **95**, 1170 (1962).
134. E. Weiss and W. Hübel, *Chem. Ber.* **95**, 1179 (1962).

Reactions of Organotin Hydrides with Organic Compounds

HENRY G. KUIVILA

Department of Chemistry, College of Technology,
University of New Hampshire, Durham, New Hampshire

I. Introduction	47
A. Nomenclature	47
B. Preparation and Properties of Organotin Hydrides	48
II. Reactions with Organic Compounds	52
A. Introduction	52
B. Additions to Alkenes and Alkynes	53
C. Reduction of Aldehydes and Ketones	66
D. Reduction of Alkyl and Aryl Halides	70
E. Reduction of Acyl Halides	81
F. Reaction with Carboxylic Acids	82
G. Other Reactions	85
References	85

I

INTRODUCTION

The compound SnH_4 was first prepared by Paneth and Furth in a yield of a few thousandths of one per cent in 1919 (1). The next three decades saw only sporadic investigations of the chemistry of SnH_4 and of its organic derivatives. During the past decade, investigators in several countries, notably van der Kerk and his collaborators in the Netherlands, began intensive research which has revealed a number of intriguing results of theoretical and practical interest. An important prelude to these investigations was the discovery by Schlesinger *et al.* in 1947 that organotin halides could be reduced to organotin hydrides in good yields by lithium aluminum hydride.

A. Nomenclature

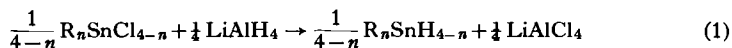
Although the parent compound is usually called "stannane," the Chemical Abstracts nomenclature emphasizes the metallic character of tin. Ac-

cordingly the compound is referred to as "tin hydride." Its organic derivatives, the organotin hydrides, are named similarly: $(\text{CH}_3)_3\text{SnH}$ is trimethyltin hydride, $(\text{C}_6\text{H}_5)_2\text{SnH}_2$ is diphenyltin dihydride, and $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{H})\text{Cl}$ is di-*n*-butylchlorotin hydride. The hydride nomenclature will be used in this chapter.

B. Preparation and Properties of Tin Hydrides

Tin hydride has been made by the reaction of hydrochloric acid with magnesium-tin alloy (1) or metallic tin (2); by reduction of stannous salts: electrolytically (3), by metals (4, 5), or sodium borohydride (6); and by reduction of stannic chloride by atomic hydrogen (7) or metals (8). Perhaps the most practical method involves the reduction of stannic chloride with lithium aluminum hydride under nitrogen (9, 10, 11) containing 0.1% oxygen (12) at -70°C . The presence of oxygen inhibits the decomposition, which ordinarily occurs at room temperature. This inhibition is at least partially due to the fact that metallic tin is a catalyst for the decomposition, but in the presence of oxygen becomes coated with a film of oxide, which is ineffective as a catalyst (12).

Reduction with lithium aluminum hydride, Eq. (1), can be extended to the preparation of a wide variety of organotin hydrides, and is generally



the most convenient laboratory preparation (10, 13, 14, 15, 16). Yields are high except in those cases in which decomposition of the hydride occurs during isolation; it is very probable that the reaction of Eq. (1) proceeds quantitatively in most cases. It is conducted by adding the organotin halide to the hydride in a suitable solvent, usually diethyl ether, at room temperature or below, followed by stirring for an hour or two. The excess lithium aluminum hydride is destroyed by addition of water, the resulting organic layer is dried, the ether removed, and the organotin hydride isolated, usually by distillation. Considine and Ventura have shown that bis(tri-*n*-butyltin) oxide can be reduced in high yield to tri-*n*-butyltin hydride by lithium aluminum hydride (17). This is advantageous because the pure oxide is less expensive than the pure chloride. Presumably this method could be extended to other organotins with electronegative substituents on the tin atom, such as alkoxides, carboxylates, or sulfides.

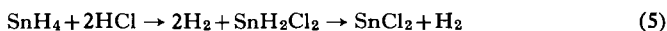
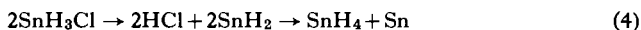
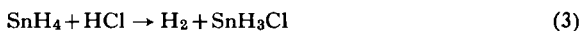
Neumann and Niermann have shown that organotin halides are reduced

to the corresponding hydrides smoothly at 0° C by diethyl- and diisobutylaluminum hydrides in high yields according to Eq. (2) (18–21). Ethoxytriethyltin and tetraethoxytin are also reduced to the hydrides by diethylaluminum hydride.

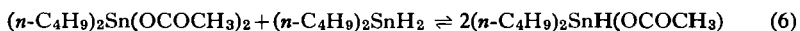


Less satisfactory methods for preparation of the simple organotin hydrides include reduction of organotin halides with amalgamated aluminum and water (22), and the reaction of organotin sodium compounds with ammonium bromide in liquid ammonia (23, 24).

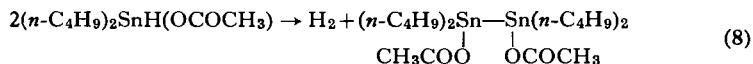
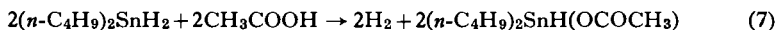
Tin hydrides containing an electronegative group attached to the tin atom are relatively unstable, and only three appear to be known. Amberger (25) prepared chlorotin trihydride by the reaction of tin hydride with hydrogen chloride at –70° C, Eq. (3); it is unstable even at this temperature and decomposes to metallic tin, stannous chloride, and hydrogen, Eqs. (4–5). Alternative mechanisms for the decomposition can be visualized.



Sawyer and Kuivila (26–28) have obtained evidence for the existence of di-*n*-butylacetoxystin hydride. When di-*n*-butyltin dihydride and di-*n*-butyltin diacetate are mixed, the infrared spectrum shows a tin–hydrogen stretching frequency at 1875 cm^{–1} in addition to that of the dihydride at 1835 cm^{–1}. The relative intensities of these bands depend on temperature, suggesting the presence of the equilibrium shown in Eq. (6). The same

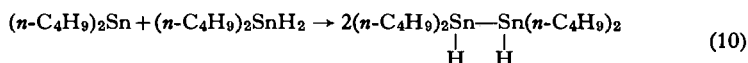
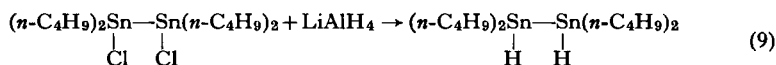


mixture can be obtained by the reaction of di-*n*-butyltin dihydride and acetic acid, Eq. (7). Upon prolonged standing at room temperature another mole of hydrogen and tetra-*n*-butylditin diacetate are formed, Eq. (8).

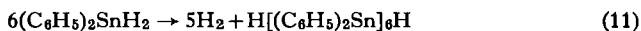


When di-*n*-butylchlorotin hydride is prepared by a reaction analogous to that of Eq. (6), there is no indication of the presence of di-*n*-butyltin dihydride, indicating that formation of di-*n*-butylchlorotin hydride is substantially complete (29).

Hydrides containing a tin-tin bond have been prepared. Ditin hexahydride is formed in about 0.1% yield, along with about 1.9% of tin hydride, by the addition of aqueous potassium stannite and potassium borohydride to aqueous hydrochloric acid (30, 31). Complete decomposition occurs below room temperature. Tetra-*n*-butylditin dihydride, prepared by the reaction of Eq. (9) or Eq. (10),¹ is considerably more stable at room tem-



perature (32). Greater stability is observed if the chain of tin atoms is lengthened: diphenyltin dihydride decomposes in methanol, Eq. (11), to



produce a hydride whose analysis and molecular weight suggest a chain of six tin atoms (33-35) which is quite stable at room temperature particularly in the dark (36). Alkyltin dihydrides display similar behavior when stirred with finely divided tin metal (18) or when heated at 100° C (32). The cause of the remarkable stability of these polytin dihydrides remains to be determined.

Organotin hydrides which have been prepared to date are listed in Table I.

The boiling points of the organotin hydrides are invariably higher than those of the corresponding hydrocarbons; *n*-butyltin trihydride boils at 100° C, for example, while *n*-pentane boils at 36° C. Melting points, on the other hand, are likely to be lower; triphenyltin hydride melts at 26-28° C, whereas triphenylmethane melts at 92.5° C.

Reactions of organotin hydrides can be monitored conveniently by taking advantage of the presence of the very strong Sn-H absorption band in the infrared spectrum in the region between 1790 cm⁻¹ and 1880 cm⁻¹. The specific location of the band is indicated for each of the hydrides in Table I. Replacement of an alkyl group on the tin atom by hydrogen leads to shift to higher frequency, as is observed for the C-H stretch in the case of alkanes. Similarly, replacement of hydrogen by chlorine or acetoxy results in a shift to higher frequencies, whereas replacement by tin results in a shift to lower frequencies.

¹ This equation is written on the basis of the infrared spectrum of the reaction mixture. The Sn-H stretch at 1795 cm⁻¹ could also be due to a polytin dihydride analogous to the product of Eq. (11).

TABLE I
 ORGANOTIN HYDRIDES

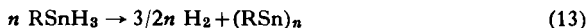
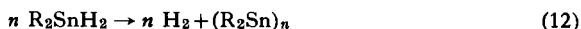
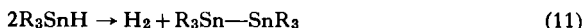
Formula	B.p. (° C)	Pressure (mm)	Sn-H band (cm ⁻¹)	References
SnH ₄	-52	760	1910	(11)
CH ₃ SnH ₃	0	760	1875	(9, 12, 13)
(CH ₃) ₂ SnH ₂	35	760	1856	(9, 37)
(CH ₃) ₃ SnH	59	760	1825	(9, 32)
C ₂ H ₅ SnH ₃	35	760	1869	(12, 15, 19)
(C ₂ H ₅) ₂ SnH ₂	99	760	1822	(15, 19)
(C ₂ H ₅) ₃ SnH	51.2-52	20	1800	(15, 16, 19)
(<i>n</i> -C ₃ H ₇) ₂ SnH ₂	39-40.5	12	~1830	(14, 16, 38)
(<i>n</i> -C ₃ H ₇) ₃ SnH	76-82	12	1820	(14, 16)
<i>n</i> -C ₄ H ₉ SnH ₃	99-101	760	1855	(14, 16, 19)
(<i>n</i> -C ₄ H ₉) ₂ SnH ₂	75-76	12	1835	(14, 16, 19)
(<i>n</i> -C ₄ H ₉) ₃ SnH	76-81	0.7-0.9	~1815	(14, 16, 32)
<i>i</i> -C ₄ H ₉ SnH ₃	87-89	760	1855	(21)
(<i>i</i> -C ₄ H ₉) ₂ SnH ₂	57-59	12	1845	(21)
(<i>i</i> -C ₄ H ₉) ₃ SnH	101-104	12	1810	(21)
C ₆ H ₅ SnH ₃	57-64	105-108	1880	(19)
(C ₆ H ₅) ₂ SnH ₂	89-93	0.3	1855	(19)
(C ₆ H ₅) ₃ SnH	168-172	0.5	1840	(16, 32)
(<i>n</i> -C ₄ H ₉) ₂ Sn $\begin{smallmatrix} \text{H} \\ \text{Cl} \end{smallmatrix}$	— ^a	—	1853	(29)
(<i>n</i> -C ₄ H ₉) ₂ Sn $\begin{smallmatrix} \text{H} \\ \text{OCOCH}_3 \end{smallmatrix}$	— ^a	—	1880	(28)
H ₃ SnSnH ₃	— ^a	—	1840	(31)
(<i>n</i> -C ₄ H ₉) ₂ Sn—Sn(<i>n</i> -C ₄ H ₉) ₂ H H	— ^a	—	1795	(32)
H[(C ₆ H ₅) ₂ Sn] ₆ H	— ^a	—	1790	(34)

^a Not determined.

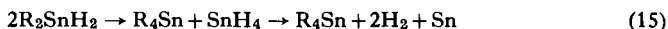
Thermal stability of organotin hydrides depends strongly on structure. For alkyl or aryl substitution the order of increasing stability is SnH₄ < RSnH₃ < R₂SnH₂ < R₃SnH. Alkyl substitution confers greater stability than aryl. Electronegative groups such as chloro or acetoxy on the tin atom result in decreased stability (26-29). The decomposition reaction is extremely sensitive to catalysis by amines (35, 36, 39, 40), silicone stopcock

grease (19), metallic tin (18, 19), aluminum halides (19), metallic surfaces (19), diborane (41), or adventitious impurities (18, 32). For this reason vessels in which these compounds are stored should be scrupulously clean.

The course of the decomposition appears to depend upon conditions. Catalysis by amines results in the formation of hydrogen and compounds containing tin-tin bonds, Eqs. (11-13). Catalysis by aluminum halides, on



the other hand, leads to more deep-seated transformations, formulated by Neumann and Niermann as follows, Eqs. (14-16).



If trimethyltin hydride is left exposed to the air, crystals of trimethyltin hydroxide begin to appear after several hours, and continue to appear for several days until the oxidation is complete. Oxide begins to appear somewhat sooner in the case of a dihydride, presumably because of its very low solubility in the hydride. Because of this susceptibility to oxidation, operations involving the hydrides are normally carried out in an inert atmosphere.

Organotin compounds in general are toxic, but none are extremely so. Precautions should be taken to avoid inhalation of vapors, or contact with the skin, particularly when working with monohydrides.

II

REACTIONS WITH ORGANIC COMPOUNDS

A. Introduction

The study of the reactions of organotin hydrides with organic compounds can be said to be in its infancy. It will be seen from the following discussion that none of the reactions has been examined in great detail as regards scope

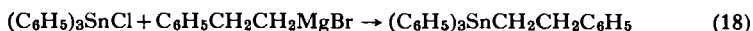
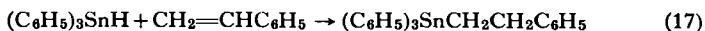
and mechanism; some have been merely noted and remain largely unexplored. The course of reactions and variation in reactivity as a function of changes in the structure of organotin hydride would be expected to depend on a number of factors: the electronegativity of the orbital of the tin atom involved in bonding to hydrogen, which will depend in turn on the substituents present on the tin atom; the bond dissociation energy of this bond, particularly in free radical reactions; steric factors which are apparently dominant in some cases; and the availability of vacant *d* orbitals on the tin atoms. In some cases it may be possible to assign a predominant role to one or another of these factors, but, in general, the relative importance of individual factors cannot be assessed at this time.

B. Additions to Alkenes and Alkynes

1. Scope

In 1947 three groups of investigators working independently reported that silanes add to olefins at high temperatures or under the influence of appropriate catalysts (41–43). The same reaction involving germanes was reported in 1954 (44). Early workers were unable to effect a benzoyl peroxide-catalyzed addition of triphenyltin hydride to triphenylallyltin (45) or to 1-octene under the catalytic influence of light, benzeneazotriphenylmethane, or benzoyl peroxide (46). On the other hand, uncatalyzed addition of this hydride to a number of olefins was found to occur readily, and in high yield, by van der Kerk and his associates (47–50). The reaction usually goes to completion with terminal olefins when the reactants are heated to about 90° C for a few hours. Olefins which have been used are listed in Table II along with yields and melting or boiling ranges of products.

The direction of addition to the double bond has been established in a few cases (48). For example, the adduct obtained from styrene, Eq. (17), is identical to the product of reaction between 2-phenylethylmagnesium bromide and triphenyltin chloride, Eq. (18). Similarly, the adduct obtained from



1-octene is identical with the product of the reaction between triphenyltin chloride and 1-octylmagnesium bromide. Indirect, but convincing, evidence that the tin adds to the terminal carbon of acrylonitrile is available. The product obtained is different from that obtained by the decarboxylation of

TABLE II
TRIPHENYL TIN HYDRIDE-OLEFIN REACTIONS

Olefin	Adduct		Reference
	Yield (%)	M.p. (° C)	
$\text{CH}_2=\text{CH} \cdot \text{CN}$	94	93-94	(48)
$\text{CH}_3-\text{CH}=\text{CH} \cdot \text{CN}$	89	103-104	(48)
$\text{CH}_2=\text{CH} \cdot \text{CH}_2 \cdot \text{CN}$	73	80-81	(48)
$\text{CH}_2=\text{CH} \cdot \text{CO}_2\text{CH}_3$	95	46.5-47	(48)
$\text{CH}_2=\text{CH} \cdot \text{CO}_2\text{H}$	94	320	(48)
$\text{CH}_2=\text{CH} \cdot \text{CO} \cdot \text{NH}_2$	90	123-124	(48)
$\text{CH}_2=\text{CH} \cdot \text{CH}(\text{OEt})_2$	~85	35.5-37.5	(48)
$\text{CH}_2=\text{CH} \cdot \text{CH}_2 \cdot \text{OH}$	93	105	(48)
$\text{CH}_2=\text{CH} \cdot \text{OC}_6\text{H}_5$	89	82.5-83	(48)
$\text{CH}_2=\text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_3$	100	45.5-46	(48)
$\text{CH}_2=\text{CH}-\text{N} \begin{array}{c} \diagup \\ \text{ } \\ \diagdown \end{array} \begin{array}{c} \text{ } \\ \text{ } \\ \text{O} \end{array}$	78	74-76	(48)
$\text{CH}_2=\text{CHC}_6\text{H}_5$	82	127-127.5	(48)
$\text{CH}_2=\text{CH} \cdot \text{C}_6\text{H}_{13}$	72	54-55	(48)
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	56	— ^a	(49)
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$	41	100-102	(49)
$\text{CH}_2=\text{CHCH}_2\text{OCOCH}_3$	42	65-66	(49)
$\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CN}$	50	59-61	(49)
$\text{CH}_2=\text{CHCH}_2\text{NHCOCH}_3$	35	95-98	(49)
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{COCH}_3$	39	70-71	(49)
$\text{CH}_2=\text{CHCH}_2\text{Sn}(\text{C}_6\text{H}_5)_3$	18	182-185	(49)
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{NHCOCH}_3$	98	154-155	(49)
$\text{CH}_2=\text{CH}-\text{C}_5\text{H}_4\text{N}$	83	112-113	(49)
$\text{CH}_2=\text{CH}-\text{N} \begin{array}{c} \diagup \\ \text{ } \\ \diagdown \end{array} \begin{array}{c} \text{ } \\ \text{ } \\ \text{ } \end{array}$	93	207	(49)

Continued.

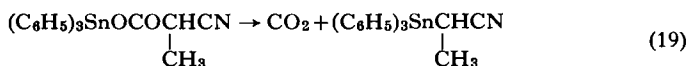
TABLE II (continued).

Olefin	Adduct		Reference
	Yield (%)	M.p. (° C)	
$\text{CH}_2=\text{CHSn}(\text{C}_6\text{H}_5)_3$	50	208–209	(50)
$\text{CH}_2=\text{CHGe}(\text{C}_6\text{H}_5)_3$	32	210–211	(50)
$\text{CH}_2=\text{CHSi}(\text{C}_6\text{H}_5)_3$	54	207–208	(50)
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{Ge}(\text{C}_6\text{H}_5)_3$	80	201–203	(61)
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{Sn}(\text{C}_6\text{H}_5)_3$	81	184–186	(61)
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{Pb}(\text{C}_6\text{H}_5)_3$	85	177–179	(61)
$\left[(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4)_2 \right] \text{Ge}(\text{C}_6\text{H}_5)_2^b$	90	207–209	(61)
$\left[(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4)_2 \right] \text{Sn}(\text{C}_6\text{H}_5)_2^b$	77	183–185	(61)
$\left[(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4)_2 \right] \text{Pb}(\text{C}_6\text{H}_5)_2^b$	89	180–182	(61)
$p\text{-C}_6\text{H}_5(\text{CH}=\text{CH}_2)_2^b$	40	136–142	(49)
$(\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_2)_2^b$	30	93–94	(49)
$(\text{CH}_2=\text{CHCO})_2\text{O}^b$	60	182–186	(49)
$(\text{CH}_2=\text{CHCOOCH}_2)_2^b$	91	93–96	(49)
$(\text{CH}_2=\text{CHCH}_2)_2\text{O}^b$	33	105–108	(49)

^a B.p. 173–176° C/0.002 mm.^b Two moles of hydride used. Data for 2:1 adduct.

the triphenyltin salt of 2-cyanopropionic acid, Eq. (19). Furthermore, the chemistry of the adduct is consistent with that of a β -cyanoethyl derivative rather than an α -cyanomethyl derivative. In the latter type of compound the tin-carbon bond is cleaved with great ease by nucleophilic or electrophilic reagents. The triphenyltin hydride-acrylonitrile adduct can be hydrolyzed to the carboxylic acid salt by boiling with alcoholic sodium hydroxide (51,

52), whereas cyanomethyltriphenyltin reacts to form triphenyltin hydroxide under similar conditions (53). Parallel arguments have been used in establishing the structure of adducts involving ethyl acrylate and acrylic acid.



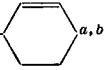
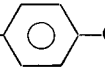
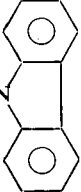
The structures of other adducts are assigned on the basis of analogy with these examples: The tin atom is assumed to be attached to the terminal carbon atom of the carbon chain. Since this is the case for ethylenes substituted by groups with different electronic effects, such as cyano, *n*-hexyl, phenoxy, and 4-pyridyl, steric effects have been said to play a predominant role in determining the direction of addition (54).

Trialkyltin hydrides undergo thermal addition also, but the only cases reported thus far involve terminal olefins substituted by the phenyl group or an electron-withdrawing group such as cyano. Examples are listed in Table III. Catalysis by platinized carbon or chloroplatinic acid has not been observed. On the other hand, azobisisobutyronitrile has proven to be an effective catalyst for the addition of organotin hydrides to nonactivated olefins (20, 21). The reactions proceed in generally good yield in 1 to 45 hours at temperatures ranging from 40° to 110° C, depending on the nature of substitution in the olefins. Electronegative substituents have a distinct activating effect. Other catalysts which have been shown to be effective for the addition of triethyltin hydride to methyl acrylate are di-*t*-butyl peroxide, benzyl hyponitrite ($\text{C}_6\text{H}_5\text{CH}_2\text{ON}=\text{NOH}$), and the methyl and ethyl esters of azobisisobutyric acid (21). Both the thermal- and radical-initiated reactions occur readily only with terminal olefins. Exceptions include cinnamonnitrile (49), β -styrenyltriphenyltin (49), methyl crotonate (49), and bicyclo[2,2,1]hepta-2,5-diene (32).

The addition reaction goes much more smoothly with acetylenes than with olefins. For example, tri-*n*-propyltin hydride reacts smoothly with propargyl alcohol in the absence of a catalyst, but not with allyl alcohol. Results are summarized in Table IV. Since the adduct still contains a double bond, further addition leading to the formation of a product containing two tin atoms is possible, and has been shown to occur with acetylene and phenylacetylene. Since olefins are less reactive, the reaction can be interrupted after the first step.


This reaction, which can be called hydrostannation, is perhaps the most valuable one among those undergone by organotin hydrides. It provides a

TABLE III
 TRIALKYLTIN HYDRIDE-OLEFIN REACTIONS

Olefin	Yield (%)	B.p. (°C)	Pressure (mm)	Reference
$(C_2H_5)_3SnH$				
$CH_2=CH(CH_2)_7COOC_2H_5^a$	78	110	0.001	(21)
$CH_2=CHCH_2OH^a$	89	128-130	12	(21)
$CH_2=CH(CH_2)_5CH_3^a$	79	145-148	12	(21)
$CH_2=CHOCOCH_3^a$	65	52-56	0.0001	(21)
$CH_2=CHCH_2OCOCH_3^a$	83	130-132	10	(21)
$CH_2=CHOC_2H_5^a$	65	98	11	(21)
$CH_2=CHOC_4H_9-n^a$	86	114-120	12	(21)
$CH_2=CHCH_2CH_2CH_2OH^a$	59	122	14	(21)
$CH_2=CH(CH_2)_7CH_3^a$	68	166-169	13	(21)
$CH_2=CHC_6H_5^a$	48	110-120	10	(21)
$CH_2=CH(CH_3)C_6H_5^a$	79	152-157	13	(21)
$CH_2=CH-$  a,b	53	81.5	0.2	(21)
$CH_2=CH-$  $-CH=CH_2^{a,b}$	37	107-109	0.001	(21)
$(CH_2=CHCH_2-)_2^a$	72 ^c	115-119	13	(21)
$CH_2=CHCH_2OCH_2CH(CH_2OH)CH_2NH_2^a$	78	80-100	0.001-0.0001	(21)
$CH_2=CHCOOCH_3^a$	93	117-119	11	(21)
$CH_2=CH(CH_3)COOCH_3^a$	80	120-122	10	(21)
$CH_2=CHCONH_2^a$	75	132-134	0.15	(21)
$CH_2=CH(CH_3)CONH_2^a$	67	136-138	0.001	(21)
$CH_2=CHCN^a$	86	128-130	12	(21)
$CH_2=CH-N$  a	82	205-210	0.001	(21)

Continued.

TABLE III (continued).

Olefin	Yield (%)	B.p. (° C)	Pressure (mm)	Reference
<i>(n</i> -C ₃ H ₇) ₃ SnH				
CH ₂ =CHCN	72	157-160	12	(48)
CH ₂ =CHCO ₂ CH ₃	63	145-150	12	(48)
CH ₂ =CHCONH ₂	77	155-161	0.4	(48)
CH ₃ CH=CHCOOC ₂ H ₅	40	111-112	0.6	(49)
CH ₂ =CHCH ₂ COOC ₂ H ₅	30	117-119	0.7	(49)
CH ₂ =CHCH ₂ CN	53	78-79	0.001	(49)
CH ₂ =CHC ₆ H ₅	86	118-121	0.007	(49)
NCCH=CHC ₆ H ₅	83	130-141	0.0003	(49)
CH ₂ =CH- 	64	121-125	0.0009	(49)
<i>(n</i> -C ₄ H ₉) ₃ SnH				
CH ₂ =CHCN	70	132-138	0.2	(48)
CH ₂ =CHCO ₂ CH ₃	84	140-141	0.4	(48)
CH ₂ =CHOC ₄ H ₉ - <i>i</i> ^{a, b}	86	105-107	0.25	(21)
CH ₂ =CHCH ₂ OH ^{a, b}	89	173-176	12	(21)
(CH ₂ =CHCH ₂) ₂ ^a	68 ^a	190-200	0.001	(21)
(CH ₂ =CHCH ₂) ₂ ^a	63 ^e	123-126	0.3	(21)
<i>(i</i> -C ₄ H ₉) ₃ SnH				
CH ₂ =CH(CH ₂) ₅ CH ₃ ^a	81	111-114	0.2	(21)
CH ₂ =CHCH ₂ OCOCH ₃ ^a	91	105-107	0.15	(21)
CH ₂ =CHOC ₄ H ₉ - <i>n</i> ^a	80	108-110	0.6	(21)
CH ₂ =CH(CH ₃)COOCH ₃ ^a	97	97-99	0.3	(21)

^a About 2 mole-% AIBN as catalyst; olefin used in 100% excess except where noted.^b Equimolar quantities of hydride and olefin used.^c Diadduct (b.p. 140-150° C at <0.001 mm) formed in 20% yield.^d Diadduct (b.p. 190-200° C at <0.001 mm) formed in 20% yield.^e Diadduct (b.p. 200-210° C at <0.001) formed in 31% yield.

pathway for the preparation of a large number of functional organotin compounds which might not be obtainable in other ways.

Certain limitations have been noted. Allyl bromide (48), crotyl chloride (56), and α -methylallyl chloride (56) undergo reduction to the corresponding alkenes, rather than addition to the double bond, upon reaction with triphenyltin hydride. Similarly, propargyl bromide (55) is reduced by tri-*n*-butyltin hydride. The presence of amino groups in the olefin may in some

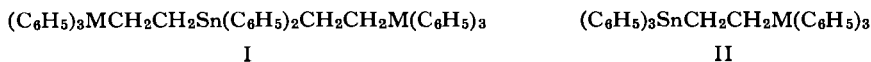
cases lead to decomposition of the hydride instead of addition (37, 38, 48). Triphenyltin hydride adds to acrylic acid,¹ but tri-*n*-propyltin hydride reacts with the carboxylic acid group to form hydrogen and tri-*n*-propyltin acrylate. *p*-Nitrostyrene suffers reduction of the nitro group in preference to addition to the double bond (54), and methyl vinyl ketone is reduced to methyl vinyl carbinol (although 1-hexene-4-one undergoes addition) (49).

TABLE IV
ADDUCTS FROM ACETYLENES AND TRIPHENYL TIN
HYDRIDE AND TRIALKYL TIN HYDRIDES

Adduct	Yield	M.p. (° C)	B.p. (° C)	Pressure (mm)	Reference
(C ₆ H ₅) ₃ SnCH=CHC ₆ H ₅	94	119–120	—	—	(49)
(C ₆ H ₅) ₃ SnCH=CHCH ₂ OH	51	115–125	—	—	(49)
(<i>n</i> -C ₃ H ₇) ₃ SnCH=CHC ₆ H ₅	75	—	119–120	0.0001	(49)
(<i>n</i> -C ₃ H ₇) ₃ SnCH=CHC ₄ H ₉	82	—	75–80	0.1	(49)
(<i>n</i> -C ₃ H ₇) ₃ SnCH=CHCH ₂ OH	34	—	120–122	0.006	(49)
(C ₆ H ₅) ₃ SnCH ₂ CH ₂ Sn(C ₆ H ₅) ₃	42	206–207	—	—	(49)
(C ₆ H ₅) ₃ SnCH ₂ CHC ₆ H ₅ Sn(C ₆ H ₅) ₃	49	139–140	—	—	(49)
(C ₆ H ₅) ₃ SnCH ₂ CH(CO ₂ CH ₃)- Sn(C ₆ H ₅) ₃	52	111–112	—	—	(49)
(<i>n</i> -C ₃ H ₇) ₃ SnCH ₂ CH(CO ₂ CH ₃)- Sn(<i>n</i> -C ₃ H ₇) ₃	69	—	120–123	0.0002	(49)
(<i>n</i> -C ₄ H ₉) ₃ SnCH=CH ₂	81	—	88	0.8	(55)

Other reducible functions, such as cyano, carboalkoxy, amido, and acyloxy do not appear to interfere, as is evident from the examples of addition which have been cited.

Diphenyl- and dialkyltin dihydrides add to olefins, as indicated by the examples in Table V.² It is striking that one mole of methyl acrylate reacts



¹ The expected product, (C₆H₅)₃SnCH₂CH₂COOH, apparently undergoes an intra-molecular electrophilic displacement by the proton to form benzene and solid with the empirical formula (C₆H₅)₂SnCH₂CH₂COO.

² Diphenyltin dihydride reacts with the vinyltriphenyl metals of silicon, germanium, and tin in an abnormal manner. Instead of the expected product, I, Compound II is formed in yields of 20–25%.

TABLE V

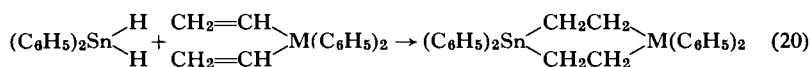
ADDUCTS FROM ORGANOTIN DI- AND TRIHYDRIDES AND OLEFINIC COMPOUNDS

Adduct	Yield (%)	M.p. (°C)	B.p. (°C)	Pressure (mm)	Reference
$(C_2H_5)_2Sn(CH_2CH_2COOCH_3)_2^{a,b}$	86	—	150–156	0.001	(21)
$(C_2H_5)_2Sn[CH_2CH(CH_3)COOCH_3]_2^{a,b}$	95	—	123–127	0.03	(21)
$(C_2H_5)_2Sn(CH_2CH_2CN)_2^{a,b}$	54	—	144–147	2.5	(21)
$(C_2H_5)_2Sn(CH_2CH_2C_6H_5)_2^{a,b}$	85	—	142–146	0.001	(21)
$(C_2H_5)_2Sn(CH_2CH_2CH_2OCH_2CH_2OH)_2^{a,b}$	55	—	170–177	0.001	(21)
$(C_2H_5)_2Sn(H)CH_2CH(CH_3)COOCH_3^{a,c}$	33	—	63–65	0.5	(21)
$(n-C_3H_7)_2Sn(CH_2CH_2C_6H_5)_2^b$	82	—	172	0.015	(49)
$(n-C_3H_7)_2Sn(CH_2CH_2CO_2CH_3)_2^b$	60	—	119–121	0.001	(49)
$(n-C_3H_7)_2Sn(CH_2CH_2CN)_2^b$	43	—	113–117	0.0004	(49)
$(n-C_4H_9)_2Sn(CF_2CF_2H)_2$	28	—	46–47	0.2	(57)
$(i-C_4H_9)_2Sn(CH_2CH_2CN)_2^{a,d}$	96	—	146–150	<0.001	(21)
$(i-C_4H_9)_2Sn(CH_2CH_2C_6H_5)_2^{a,e}$	83	—	185–189	<0.001	(21)
$(i-C_4H_9)_2Sn(CH_2CH_2COOCH_3)_2^{a,e}$	93	—	117–120	<0.001	(21)
$(i-C_4H_9)_2Sn[CH_2CH(CH_3)COOCH_3]_2^{a,e}$	89	—	102–103	<0.001	(21)
$(C_6H_5)_2Sn(CH_2CH_2CO_2CH_3)_2^b$	34	—	191–194	0.003	(49)
$(C_6H_5)_2Sn[CH_2CH_2-\text{C}_6\text{H}_4-\text{Ge}(C_6H_5)_3]_2^d$	79	168–169	—	—	(61)
$(C_6H_5)_2Sn[CH_2CH_2-\text{C}_6\text{H}_4-\text{Sn}(C_6H_5)_3]_2^d$	84	75	—	—	(61)
$(C_6H_5)_2Sn[CH_2CH_2-\text{C}_6\text{H}_4-\text{Pb}(C_6H_5)_3]_2^d$	81	70	—	—	(61)
$(C_6H_5)_2Sn[CH_2CH(CH_3)COOCH_3]_2^{a,b}$	95	—	180–185	0.01	(21)
$n-C_3H_7Sn(CH_2CH_2CO_2CH_3)_3^b$	11	—	136–140	0.0008	(49)
$n-C_4H_9Sn(CH_2CH_2CO_2CH_3)_3^b$	82	—	139–141	0.0004	(49)
$n-C_4H_9Sn[CH_2CH(CH_3)COOCH_3]_3^{a,b}$	75	—	150–155	0.001	(21)
$i-C_4H_9Sn[CH_2CH(CH_3)COOCH_3]_3^{a,b}$	86	—	165–167	0.01	(21)
$i-C_4H_9Sn[CH_2CH_2COOCH_3]_3^{a,b}$	95	—	150–153	0.0001	(21)

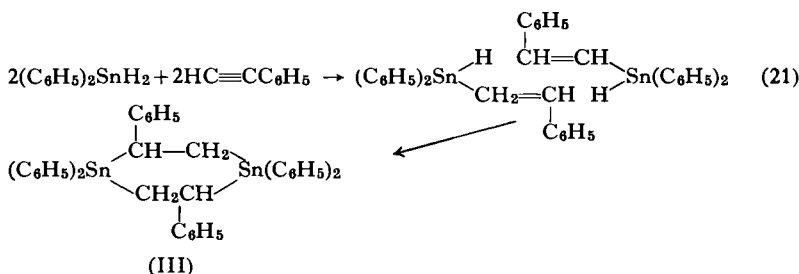
^a About 2 mole-% of azobisisobutyronitrile used as catalyst.^b (Olefin/hydride ratio) = 3.^c (Olefin/hydride ratio) = 1.^d (Olefin/hydride ratio) = 2.^e (Olefin/hydride ratio) = 2.5.

with one mole of dihydride to form $(n\text{-C}_3\text{H}_7)_2\text{Sn}(\text{CH}_2\text{CH}_2\text{COOCH}_3)_2$; i.e., the intermediate monohydride, $(n\text{-C}_3\text{H}_7)_2\text{Sn}(\text{H})\text{CH}_2\text{CH}_2\text{COOCH}_3$, adds more rapidly to methyl acrylate than does the dihydride. This implies that the carbomethoxy group plays a role in increasing the reactivity of the hydride, perhaps by chelation of the carbonyl oxygen with the tin atom. In the addition of diethyltin dihydride catalyzed by azobisisobutyronitrile, a 33% yield of the corresponding monoadduct has been obtained (21). *n*-Butyltin and *i*-butyltin trihydrides, in spite of relatively low thermal stability, have been shown to react with 3 moles of olefin, as indicated in Table V.

Use of dihydrides introduces the possibility of formation of cyclic or polymeric organotin compounds by appropriate choice of bifunctional reaction partners. The first example of cyclic compound formation was reported by Henry and Noltes (58), who carried out the reaction shown in Eq. 20, with M being silicon or germanium. The same reaction involving diphenyldivinyltin yielded

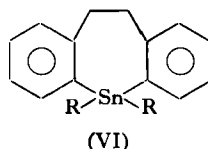
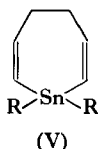
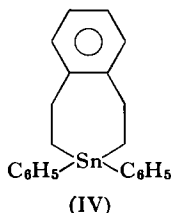


no distannacyclohexane (III). This compound could be obtained by the reaction of diphenyltin dihydride and phenylacetylene, Eq. (21).

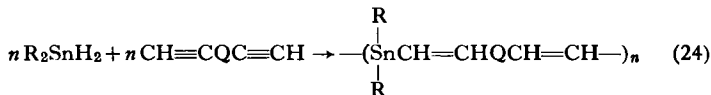
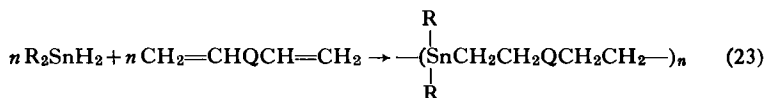
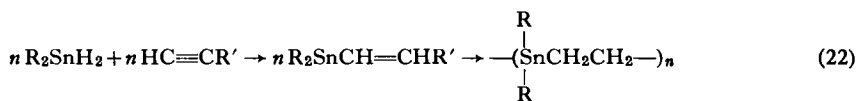


Two isomers, presumably with the phenyl groups *cis* and *trans* to each other, were obtained in comparable yields. *o*-Divinylbenzene and diphenyltin dihydride react to form 1,1-diphenyl-4,5-benzo-1-stannacycloheptene (IV), a trimer to which a cyclic structure has been assigned, and polymer (59). The reaction of 1,5-hexadiyne with R_2SnH_2 yielded 12% to 28% of the stannepin (V), when R was CH_3 , C_2H_5 , *n*- C_3H_7 , and C_6H_5 (37). Dibenzo analogs (VI) have been prepared previously by a more laborious sequence of reactions (60).

Noltes and van der Kerk have exploited the reaction of organotin dihydrides with bifunctional unsaturated compounds as a means of preparing polymers containing tin atoms in the backbone of the chain (37, 59, 61).



Reaction partners have included acetylenes, dienes, and diynes with compounds R_2SnH_2 , Eqs. (22, 23, 24), in which R is methyl, ethyl, *n*-propyl, *n*-butyl, and phenyl.





The first of these methods with di-*n*-butyltin or di-*n*-propyltin hydride and phenylacetylene gives a viscous oil; in the latter case the average value of *n* is 11 (37, 59). The polymeric adduct which is formed in the corresponding reaction involving diphenyltin dihydride is a hard, brittle solid (59).

Cyclopentadiene appears to be the only conjugated diene which has been used. It reacts with di-*n*-propyltin or diphenyltin dihydride to form a one-to-one adduct, whose structure has not been described (59). The other adducts involving di-*n*-propyltin dihydride, for example, range from viscous oils, to soft and tacky, tough, or rubbery substances, depending on the diene used. A list of the dienes is contained in Table VI.

As has been pointed out above, addition of organotin hydrides to the carbon-carbon triple bond occurs with particular facility. Reaction (24) makes possible syntheses of organometallic polymers containing unsaturation in the chain, as is the case in natural rubber. This has been realized to

some extent (59). Diethyltin dihydride and 1,5-hexadiyne react in refluxing pentane to form a rubberlike polymeric adduct. The product from diphenyltin dihydride and *p*-divinylbenzene, after heating at 160° C, also shows rubbery character, and has a molecular weight of 65,000. These and other diynes that have been used to date are included in Table VI.

TABLE VI
DIENES AND DIYNES WHICH HAVE BEEN SHOWN TO
REACT WITH ORGANOTIN DIHYDRIDES

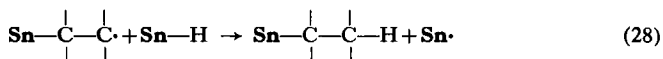
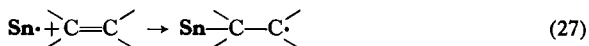
$(\text{CH}_2=\text{CHCOOCH}_2-)_2$	$p\text{-(CH}_2=\text{CH-)}_2\text{C}_6\text{H}_4$
$(\text{CH}_2=\text{CHCOOCH}_2-)_2$ CH ₃	$(\text{CH}_2=\text{CC}_6\text{H}_4\text{-}p-)_2$ CH ₃
$(\text{CH}_2=\text{CCO-})_2\text{O}$ CH ₃	$(\text{HC}\equiv\text{CCH}_2-)_2$
$(\text{CH}_2=\text{CHCH}_2\text{OOCCH}_2-)_2\text{O}$	$\text{HC}\equiv\text{C}(\text{CH}_2)_5\text{C}\equiv\text{CH}$
$\text{CH}_2=\text{CHCOOCH}_2=\text{CH}_2$	$\text{HC}\equiv\text{C}$  $\text{C}\equiv\text{CH}$
$\text{CH}_2=\text{CH}-\text{CH} \begin{array}{c} \text{O}-\text{CH}_2 \\ \text{O}-\text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH}_2-\text{O} \\ \text{CH}_2-\text{O} \end{array} \text{CHCH}=\text{CH}_2$	$(\text{CH}_2=\text{CH}$  $)_2\text{M}(\text{C}_6\text{H}_5)_2^a$

^a M=Ge, Sn, Pb.

2. Mechanism

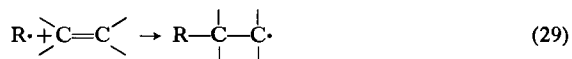
Detailed studies on the mechanisms of addition of organotin hydrides to olefins and acetylenes remain to be made. Certain inferences can be drawn, however, on the basis of information now available. The catalysis by free radical sources demonstrates that the reaction *can* proceed by a free radical chain mechanism, since only a few mole per cent of initiator is needed in many cases for complete reaction. An attractive reaction sequence is shown in Eqs. (25–28), in which R· is a carbon free radical and Sn· is a trisubstituted tin radical. Reaction (26) is the chain initiation step and reactions (27) and (28) comprise the propagation steps. Most of the characteristics of the hydrostannation reaction can be accommodated in such a scheme. For example, free radicals attack terminal olefins at the terminal carbon atom because the resulting secondary or tertiary radical is more stable than the

alternative primary one. This is true even if the vinyl group is substituted by groups so divergent in their electronic effects as phenyl, *n*-hexyl, cyano, or acetoxy.



The fact that phenyltin hydrides are more reactive than the corresponding alkyl analogs may be due to two factors. The triphenyltin radical may be more stable than a trialkyltin radical because of possible delocalization of the unpaired electron into the phenyl rings. However, this would not be expected to occur in large degree because no evidence has been found for the dissociation of hexaphenylditin into free radicals at ordinary temperatures. Another, more reasonable interpretation concerns the relative strengths of the tin-hydrogen bonds in aryl- and alkyltin hydrides. In the aryltin hydrides inductive withdrawal of electrons from the tin atom, and, consequently, from the tin-hydrogen bond, would be greater than in the case of the alkyltin hydrides. The result would be a diminution in the bond moment, and the hydride character of the hydrogen atom, as well as a decrease in the bond energy because of the decrease in its polar contribution.

There appears to be no significant indication of polymerization of the olefin, or of telomerization in hydrostannation. This is not unexpected, since the polymerization step, Eq. (29), involves the breaking of the second



bond of a carbon-carbon double bond (about 60 kcal) and formation of single carbon-carbon bond (about 80 kcal), a process which would be exothermic by about 20 kcal. On the other hand, the competing reaction of Eq. (28 or 26) involves the breaking of a tin-hydrogen bond (about 70 kcal) and formation of carbon-hydrogen bond (98 kcal), a process which is more exothermic by about 8 kcal. Since the difference between the two processes is not extreme, polymerization might be able to compete with addition if the tin hydride were so designed that the activation energy for reaction (26, 27 or 28) is somewhat larger than that for the examples reported thus far.

The fact that unsaturated halides have undergone reduction rather than hydrostannation could mean that reaction (30) is faster than reaction (27). Since carbon-halogen and tin-halogen bond energies can vary greatly, it would be expected that the rate of Eq. (30) can vary over a large range with the result that the addition reaction could be made to compete under appropriate circumstances (see Section D).

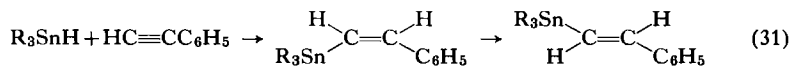


Ketones with α,β -unsaturation undergo reduction (see Section C) whereas nonconjugated unsaturated ketones undergo hydrostannation (49). Similar arguments could be invoked in this case, but would be somewhat more speculative because little is known about the mechanism of carbonyl reduction by organotin hydrides.

The ineffectiveness of certain catalysts requires comment. The substantial reducing power of organotin hydrides precludes the use of catalysts which are reduced too easily. Benzoyl peroxide and chloroplatinic acid undoubtedly fall into this category, whereas *t*-butylperoxide, azobisisobutyronitrile, and benzyl hyponitrite (21) do not. The ineffectiveness of hydroquinone as an inhibitor may be due to the fact that the organotin hydride is an even better "inhibitor," i.e., reaction (26 or 28) is much faster than the reaction which hydroquinone undergoes with the free radicals present in the system.

Although the above discussion regarding hydrostannation of olefins should be valid for the reactions initiated by free radical sources, it may not be applicable to the thermal reaction. However, all of the information currently available is consistent with a free radical mechanism in this case also.

The stereochemistry of the addition of trimethyltin and triphenyltin hydrides to phenylacetylene has been examined carefully by Fulton (62). In each case the product formed is a *cis* adduct which rearranges readily to the more stable *trans* adduct, Eq. (31). Thus a *trans* addition occurs, and a



four-center mechanism such as is probable for hydroboration is excluded. It has not yet been established clearly whether hydrostannation of acetylenes is subject to free radical catalysis, nor is it obvious why acetylenes are more reactive than olefins. This difference may be explicable in terms of a nucleophilic attack on the acetylene by the tin atom of the hydride (62).

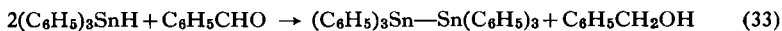
C. Reduction of Aldehydes and Ketones

1. Scope

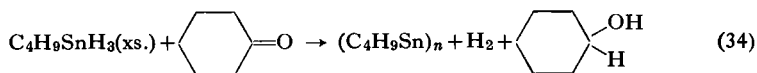
The first observation of the reduction of a ketone by an organotin hydride appears to have been the result of an attempt to carry out the hydrostannation of 2 moles of methyl vinyl ketone by 1 mole of diphenyltin dihydride (63, 64). Instead of the expected adduct the products were polymeric diphenyltin, which precipitated during the reaction, and methyl vinyl carbinol, Eq. (32). This reaction is surprising because the alcohol is isolated



from the reaction mixture rather than the alkoxide, which is the product when complex metal hydrides, such as lithium aluminum hydride, or silanes (65) are used. As a result the usual hydrolytic procedure for working up a reaction mixture can be circumvented; this is a feature which would be of value in the reduction of carbonyl compounds containing functional groups which are sensitive to acid or base. Equally remarkable is the fact that organotin monohydrides react in a similar way, as shown in Eq. (33). It is not known



for certain whether the organotin trihydrides react in the same manner, but a combination of reduction and thermal decomposition of excess hydride proceeds as shown in Eq. (34) (55). This reaction, incidentally, constituted



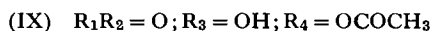
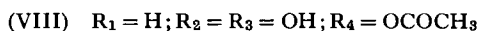
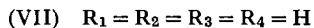
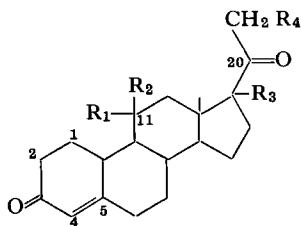
the first example of the preparation of a compound with the empirical formula, R_nSn . The relative ease with which the organotin hydrides reduce aldehydes and ketones follows the order $(\text{C}_6\text{H}_5)_2\text{SnH}_2 > (n\text{-C}_4\text{H}_9)_2\text{SnH}_2 > n\text{-C}_4\text{H}_9\text{SnH}_3 > (\text{C}_6\text{H}_5)_3\text{SnH} > (n\text{-C}_4\text{H}_9)_3\text{SnH}$. Simple carbonyls are reduced in exothermic reactions at room temperature by the dihydrides; benzaldehyde is reduced by triphenyltin hydride at 100°C in several hours, whereas tri-*n*-butyltin hydride requires a temperature of 140°C for reduction in a comparable period of time. Diphenyltin dihydride occasionally is decomposed in the presence of even simple ketones such as acetone, anthraquinone, and 2-acetylcyclohexanone. This is perhaps due, at least in part, to the presence of adventitious impurities in the samples used, since benzoquinone, cyclohexanones, and benzophenone are reduced in good yield. For

this reason, the more stable di-*n*-butyltin dihydride may be the more generally useful reducing agent. An indication of the scope of the reduction with these dihydrides is provided by the examples listed in Table VII.

TABLE VII
REDUCTIONS OF ALDEHYDES AND KETONES WITH DIPHENYLTIN
DIHYDRIDE AND DI-*n*-BUTYLTIN DIHYDRIDE

Carbonyl compound	% Alcohol with	
	(C ₆ H ₅) ₂ SnH ₂	(<i>n</i> -C ₄ H ₉) ₂ SnH ₂
Benzophenone	59	85
2-Methylcyclohexanone	83	94
4-Methylcyclohexanone	82.5	76.5
4- <i>t</i> -Butylcyclohexanone	85.5	93.5
<i>l</i> -Menthone	81.5	81.5
<i>d</i> -Carvone	83.5	70.5
Methyl vinyl ketone	59	31, 12.5
Crotonaldehyde	59	43.5
Benzoquinone	59	66
Benzil	87.5	93

Among the other simple compounds reduced by diphenyltin dihydride are cyclohexanone (82%), benzaldehyde (62%), mesityl oxide (60%), and chalcone (75%). It can be seen that the yields are high with the simple ketones and aldehydes, and moderate in the case of the α,β -unsaturated analogs. The cause of the lower yields has not been examined, but may be due to the occurrence of hydrostannation, particularly of the product alcohol, as a side reaction. In all of these cases the unsaturated alcohol was the reduction product; the double bond was not reduced. The same is true when triphenyltin hydride is used in the reduction of methyl vinyl ketone and phenyl vinyl ketone (66).

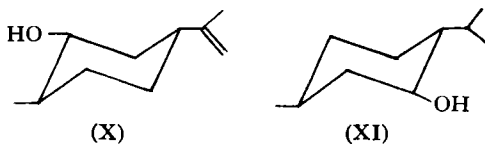


Reductions of several ketosteroids by diphenyltin dihydride have been examined as a means of discovering what kind of selectivity exists among carbonyl groups in a given molecule (67). Pregnenolone (VII) was reduced at C-3 in preference to C-20 in a ratio of about 6.5 to 1. This result stands in marked contrast to the fact that sodium borohydride reduces the keto group

TABLE VIII
STEREOCHEMISTRY OF REDUCTION OF CYCLOHEXANONES BY ORGANOTIN
HYDRIDES, COMPLEX METAL HYDRIDES, AND ALUMINUM ISOPROPOXIDE

Reducing agent	% <i>trans</i> Alcohol from		% X ^a from carvone	% XI ^a from menthone
	4- <i>t</i> -Butyl- cyclo- hexanone	4-Methyl- cyclo- hexanone		
(π -C ₄ H ₉)SnH ₃	92	73	—	—
(π -C ₄ H ₉) ₂ SnH ₂	88	75	94.7	—
(C ₆ H ₅) ₂ SnH ₂	87	76	97.1	48
(C ₆ H ₅) ₃ SnH	87	70	—	—
LiAlH ₄	91–93 ^b	79–81 ^b	94 ^c	71 ^d
NaBH ₄	—	75	—	49
Al(<i>i</i> -OPr) ₃	77–81	67	58 ^c	30
(Equilibrium)	77–81 ^b	69–71 ^b	—	—

^a Structures as follows:



^b From ref. (68).

^c From ref. (70).

^d From ref. (69).

at C-20 preferentially when there is a double bond in the 4,5-position, and provides the simplest route to the 3-hydroxy compound from the 3-ketone. Another striking result is seen in the comparison of the reductions of hydrocortisone (VIII) and cortisone (IX), which differ in the fact that the first has a tetrahedral carbon at C-11 and the latter is trigonal at this position. With one mole of diphenyltin dihydride, hydrocortisone gives 63% reduction at C-20 in addition to 14% reduction at both C-3 and C-20; cortisone, on the other hand, gives 50% reduction at C-3 in addition to 25% at both

C-3 and C-20. Thus the reduction process is extremely sensitive to the change in hybridization at C-11, which is remote from both the carbonyl groups. The C-11 carbonyl in cortisone is highly hindered, and is unaffected by diphenyltin dihydride even when used in excess. A similar effect of steric bulk shows up in the case of camphor, which could not be reduced in satisfactory yield with either diphenyltin dihydride or di-*n*-butyltin dihydride under conditions which lead to facile reduction of simple cyclohexanones (63).

TABLE IX
REDUCTION OF METHYLCYCLOHEXANONES BY
TRIPHENYLTIN HYDRIDE ^a

Ketone	% Yield of alcohol	% <i>Trans</i>
Cyclohexanone	55	—
2-Methylcyclohexanone	56	61
3-Methylcyclohexanone	43	17
4-Methylcyclohexanone	52	81

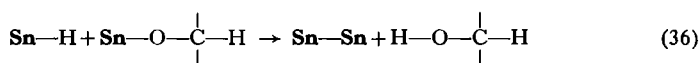
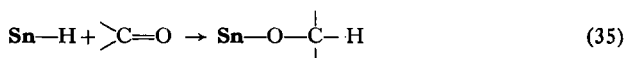
^a From ref. (71).

The stereochemistry of reduction of several ketones has been studied. Benzil with diphenyltin dihydride gives *meso*-dihydrobenzoin containing little, if any, of the *dl*-isomer. Substituted cyclohexanones have been reduced with several of the organotin hydrides. Results are presented in Tables VIII and IX. It can be seen from the data in Table VIII that there is little variation in the selectivity of the organotin hydrides as the number of hydrogen atoms changes from one to three. Also the predominant product is the more stable isomer in each case. Comparison with reductions by lithium aluminum hydride and sodium borohydride indicates that the former is more selective and the latter about as selective as the organotin hydrides. The reaction between triphenyltin hydride and 4-methylcyclohexanone reported in Table VIII was carried out at about 100° C, whereas that reported in Table IX was carried out at 150° C. This difference in temperature may account for the apparent discrepancy in the isomer distributions.

2. Mechanism

Very little is known about the mechanism of these reductions. It is clear from their stoichiometry that they are probably fairly complex. Since a given hydride reduces different ketones at different rates, the rate-determining

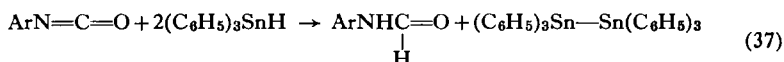
step cannot be a dissociation of the hydride. A nucleophilic attack by the hydride on the carbonyl group, as is the case with lithium aluminum hydride, is very unlikely. This follows from the fact that phenacyl bromide is reduced preferentially at the carbonyl group by lithium aluminum hydride, whereas the halogen is replaced by hydrogen preferentially with tri-*n*-butyltin hydride (see Section D). In the latter case a free radical mechanism is clearly indicated. Thus, a free radical mechanism is also a good possibility for the organotin hydride reduction of the carbonyl group. One possible reaction scheme is represented by Eqs. (35) and (36). Reaction (35) can be brought



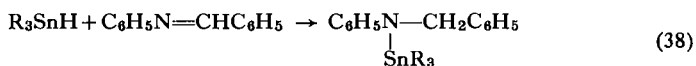
about at moderate temperatures in the presence of azobisisobutyronitrile (20, 20a) or zinc chloride (20a), and photochemically (20b, 20c). Sawyer has shown that reaction (36) and its analogs can be effected. When di-*n*-butyl-dimethoxytin is treated with di-*n*-butyltin dihydride, methanol and di-*n*-butyltin are formed. Similarly di-*n*-butyltin oxide and di-*n*-butyltin dihydride react to form water and di-*n*-butyltin (72).

Photochemical reduction in the presence of excess tin hydride can lead to either the alcohol or the pinacol (20d).

Phenyl isocyanate and α -naphthyl isocyanate are reduced selectively in 40–50% yield by triphenyltin hydride to the corresponding *N*-arylformamides, as shown in Eq. (37) (73). The isocyanates are reduced to *N*-methylamines by lithium aluminum hydride.



The only other nitrogen analogs of a carbonyl compound which appear to have been examined are benzalanilines, which undergo azobisisobutyronitrile-catalyzed addition with trialkyltin hydride (20, 20a).

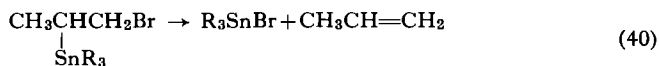
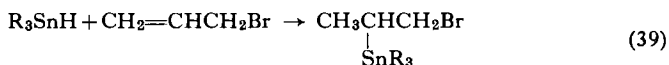


D. Reduction of Alkyl and Aryl Halides

1. Scope

As was pointed out in the discussion of hydrostannation, allylic halides undergo reduction to alkenes rather than addition to the double bond (48,

56). It was thought that this might occur by an addition-elimination mechanism as shown in Eqs. (39) and (40). It was soon shown that this is almost

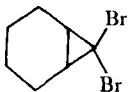
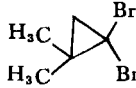
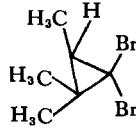
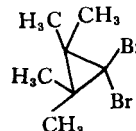
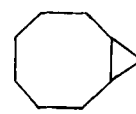
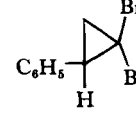
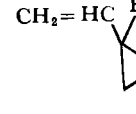
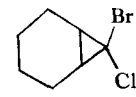


certainly not the case because: (a) the direction of addition required in Eq. (39) is opposite to that expected on the basis of known examples; (b) a substituted allylic halide should yield a single product, whereas 3-chloro-1-butene yields a mixture of 1- and 2-butenes instead of 2-butene alone; (c) simple saturated halides are reduced under comparable conditions.

Extensive study of this reaction has made it perhaps the best understood among the reactions of organotin hydrides. Aliphatic bromides react exothermally with tri-*n*-butyltin hydride in the absence of a solvent. Chlorides, even the allylic and benzylic ones, are much less reactive, requiring temperatures around 100° C for reaction in a reasonable time. Examples presented in Table X provide an indication of the scope of the reaction with this particular hydride. It is evident from the data that halides which might be expected to be unreactive, such as cyclohexyl bromide and the bromocyclopropanes, undergo facile reduction. Perhaps one of the most valuable characteristics of the reaction is its selectivity among geminal polyhalides. Benzotrichloride can be reduced successively in high yield to benzal chloride, benzyl chloride, and toluene. Similarly, carbon tetrachloride can be reduced in high yield to chloroform, which is selectively reduced in turn to methylene chloride. The geminal dihalocyclopropanes are reduced to the monohalides, but it should be noted that a mixture of the possible isomers usually results. Activation of a halide is not necessary in order for reduction to compete successfully with hydrostannation, as is indicated by the case of 1,1-dibromo-2-vinylcyclopropane. A particularly dramatic example of the dependence of reactivity on the halogen is provided by a comparison of bromocyclohexane and chlorocyclohexane: The former undergoes exothermic reduction; the latter is only partially reduced upon heating at 120° C for 40 minutes. The 7,7-dichloro- and dibromobicyclo[4,1,0]heptanes constitute another pair for comparison.

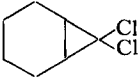
In Table XI are listed reductions which have been effected with triphenyltin hydride. The results show that α -phenylethyl chloride is reduced more readily with this hydride than with tri-*n*-butyltin hydride. Stepwise reduc-

TABLE X
REDUCTION OF HALIDES BY TRI-*n*-BUTYL TIN HYDRIDE

Halide	Conditions ^a	Yield ^b (%)	Reference
$C_6H_5CH_2Br$	4 M in ether, ex., 12 hr	68	(56)
Cyclo- $C_6H_{11}Br$	Neat, ex., 1 hr	71	(56)
<i>n</i> - $C_8H_{17}Br$	Neat, ex., 1 hr	80	(56)
$C_6H_{13}CHBrCH_3$	Neat, ex., 1 hr	78	(56)
$C_6H_5-CH_2CH_2Br$	Neat, 100° C, 4 hr	85	(32)
	Neat, ex.	82 ^c	(74)
	Neat, ex.	82	(74)
	Neat, ex.	79 ^a	(74)
	Neat, ex.	78 ^e	(74)
	Neat, ex.	84	(74)
	Neat, ex.	71	(74)
	Neat, ex.	62	(74)
	Neat, ex.	97 ^f	(74)

Continued.

TABLE X (continued).

Halide	Conditions ^a	Yield ^b (%)	Reference
CHBr ₃	Neat, ex.	62	(74)
Br ₃ CF	Neat, ex.	69	(74)
C ₆ H ₅ CCl ₃	Neat, ex., 2.5 hr	95	(32)
C ₆ H ₅ CHCl ₂	Neat, 140° C, 20 min	70	(32)
C ₆ H ₅ CH ₂ Cl	Neat, 140° C, 20 min	78	(32)
C ₆ H ₅ CHClCH ₃	Neat, 100° C, 17 hr	77	(56)
CCl ₄	Neat, ex.	85	(74)
CHCl ₃	Neat	92	(74)
Cyclo-C ₆ H ₁₁ Cl	Neat, 120° C, 40 min	36	(56)
	Neat, 140° C, 3 hr	83	(74)
<i>n</i> -C ₇ H ₁₅ I	1.5 <i>M</i> in bromobenzene, ex., 40 hr	96	(32)

^a Ex., exothermic reaction, temp. kept below 50° C.

^b Product with one halogen atom replaced by hydrogen; Br replaced in preference to Cl or F.

^c *Exo* bromide/*endo* bromide = 1.0/2.5.

^d Hydrogens: *cis/trans* = 4/1.0.

^e With 2 moles of hydride, 69% of 1,1,2,2-tetramethylcyclopropane obtained.

^f 7-Chlorobicyclo [4,1,0] heptane; *exo* chloride/*endo* chloride = 1.0/2.5.

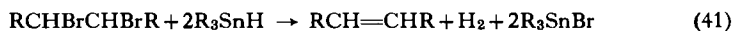
^g *Exo* chloride/*endo* chloride = 1.0/1.8.

tion of the chloromethanes has been brought about successfully by triphenyltin hydride, as indicated.

Di-*n*-butyltin dihydride reduces halides somewhat more easily than tri-*n*-butyltin hydride. Yields of reduction products isolated from typical halides are: 2-bromooctane, 99%; 1-bromooctane, 84%; bromocyclohexane, 82%; benzyl bromide, 60%; benzyl chloride, 83%; 3-bromocamphor, 79%.

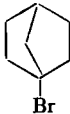
In most cases which have been examined thus far the reaction has proven to be remarkably free of complications. Except in the case of 1-bromonorbornane low yields have probably been due to incomplete reaction. In no case has there been indication of dehydrohalogenation.

Although geminal polyhalides undergo normal reduction, vicinal dibromides have been found to suffer elimination according to Eq. (41).



Tri-*n*-butyltin hydride debrominated 1,2-dibromopropane at room temperature in 3 hours, yielding 81% of propylene; *meso*-stilbene dibromide required heating to 100° C for 15 hours for complete reaction, giving 85% of *trans*-stilbene. It is not known whether this is the result of a highly selective *trans* elimination, or simply the consequence of formation of the most stable isomer (32). A dehalogenation mechanism similar to that involved in dehalogenation by metals such as zinc is unlikely because no cyclopropane is formed in the reaction of 1,3-dibromopropane with tri-*n*-butyltin hydride.

TABLE XI
REDUCTIONS OF HALIDES BY TRIPHENYLTIN HYDRIDE

Halide	Conditions	Yield (%)	Reference
$C_6H_5CHClCH_3$	Neat, ex., 18 hr	89	(56)
Cyclo- $C_3H_5CH_2Cl$	Neat, 130° C, 5 hr	< 1	(56)
	Neat, 80° C	9.3	(75)
CCl_4	Neat, ex.	100 ^a	(76)
$CHCl_3$	Neat, 70° C, 13 hr	99 ^a	(76)
CH_2Cl_2	Neat, reflux, 18 hr	92 ^a	(76)
$CH_2=C(CH_3)CH_2Cl$	—	91 ^a	(66)
<i>n</i> - C_4H_9Br	—	78 ^a	(66)
$CH_2=CHCH_2Br$	Neat, 80° C, 4 hr	98 ^a	(48)

^a Yield given is that for triphenyltin halide; yield of reduction product not determined.

Furthermore, bromohydrins do not appear to undergo elimination: 1,3-dibromo-2-propanol reacts with 2 moles of the hydride to produce 2-propanol in 85% yield (32).

α -Haloketones are cleanly reduced to the unhalogenated ketones. Tri-*n*-butyltin hydride has been shown to reduce phenacyl chloride at 150° C (71%), phenacyl bromide at room temperature (84%), and 3-bromocamphor at room temperature (61%); with triphenyltin hydride phenacyl chloride was reduced in 86% yield at 90° C. In none of these cases was there any indication of the presence of alcohol in the reaction product mixture (32). In contrast to the ketones, *p*-nitrobenzyl bromide is reduced preferentially at the nitro group by tri-*n*-butyltin hydride.

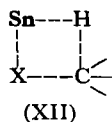
Reduction of the vinyl halide, β -bromostyrene, at 100° C with tri-*n*-butyltin hydride provided only 35% of styrene, presumably because of hydrostannation of some of the styrene under the reaction conditions. Aryl halides can be reduced satisfactorily under fairly drastic conditions (66, 77). For example, 1- and 2-bromonaphthalenes have been reduced by triphenyltin hydride in 31% and 69% yields, respectively, at 150° C in 15 hours. Several *p*-substituted halobenzenes have been studied, as shown in Table XII. There is an indication that electron-releasing substituents hinder reaction and electron-withdrawing substituents have the opposite effect. However the facilitation by the phenyl group complicates the picture.

TABLE XII
REDUCTIONS OF *p*-SUBSTITUTED HALOBENZENES
BY TRIPHENYLTIN HYDRIDE

R	X	% Tin halide formed at	
		154° C	95° C
H	Br	90	12
CH ₃	Br	91	10
OCH ₃	Br	98	7
Cl	Br	97	16
C ₆ H ₅	Br	95	23
H	I	91	84

2. Mechanism

It has been fashionable to postulate multicenter mechanisms for reactions of organometallic compounds. In the present case a four-center transition state (XII) would be an attractive one. On the other hand, by analogy with



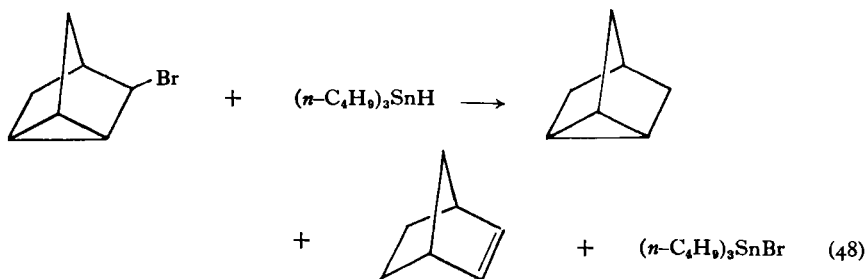
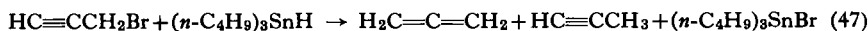
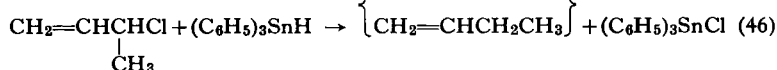
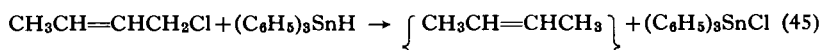
the reaction of lithium aluminum hydride, a nucleophilic displacement of the S_N2 type might be postulated. However, all of the information now available which has a bearing on mechanism is consistent only with a free radical chain mechanism. The two mechanisms mentioned above, as well as others such as the S_N1 mechanism, can be eliminated on the basis of a

variety of experimental observations which have been made. The reactions of Eqs. (42-44) comprise an attractive mechanistic hypothesis. In this

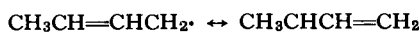


sequence $\text{Q}\cdot$ is a free radical or a molecule which is capable of abstracting a hydrogen atom from a tin hydride. Reactions (43, 44) constitute the reaction chain whose length will be determined by the nature of R and the substituents on the tin atom as well as the nature of X. Chain termination is not considered here because no information about it is currently available.

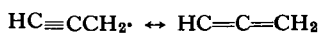
Evidence for the formation of intermediate ions or free radicals comes, first of all, from structural changes accompanying reactions of certain types of halides as shown in Eqs. (45-48) (56). The formation of a mixture of



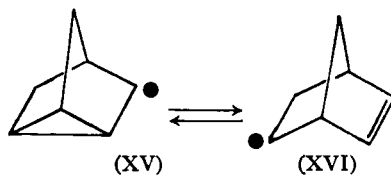
butenes in reactions (45, 46) is consistent with the intermediacy of the allylic radical, XIII; similarly the propargylic radical, XIV, would be a reasonable intermediate in reaction (47). Whereas these two radicals are resonance hybrids which could react at either end of a triad of carbon atoms, the intermediate in reaction (48) is probably not a resonance hybrid, but a mixture



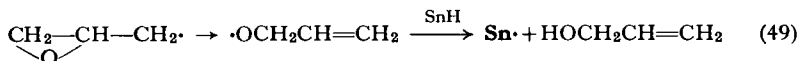
(XIII)



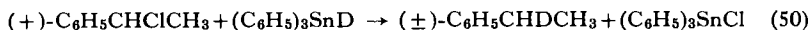
(XIV)



of two distinct species, (XV) and (XVI) (78). Rearrangement also accompanies the reduction of epibromohydrin; the major product is allyl alcohol, whose formation can be rationalized in terms of opening of the oxirane ring of the 2-oxirylmethyl radical, Eq. (49).



Further evidence comes from the fact that optically active α -phenylethyl chloride reacts with triphenyltin deuteride to produce racemic α -deuterio-phenylethane, Eq. (50) (56). These observations argue strongly against an



$\text{S}_{\text{N}}2$ or four-center mechanism, either of which would be expected to lead to a single enantiomorph. These results are the expected ones for the mechanism shown above, whereas they would follow only from an improbable combination of $\text{S}_{\text{N}}2$, $\text{S}_{\text{N}}2'$, and four-center mechanisms. The fact that reduction of the 7,7-dihalobicyclo[4,1,0]heptanes by tri-*n*-butyltin hydride leads to mixtures of 7-halobicyclo[4,1,0]heptanes also fits into the scheme above, although it could be interpreted in terms of the $\text{S}_{\text{N}}2$ or four-center mechanisms.

TABLE XIII
CATALYSIS OF HALIDE REDUCTION BY AZOBISISOBUTYRONITRILE

Halide	Solvent	Time (min)	% Reduction	
			Uncatalyzed	Catalyzed
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	$\text{C}_6\text{H}_5\text{Cl}$	30	26	100 ^a
Cyclo- $\text{C}_6\text{H}_{11}\text{Cl}$	$\text{C}_6\text{H}_5\text{CH}_3$	35	1	70 ^a
$\text{C}_6\text{H}_5\text{Br}$	$\text{C}_6\text{H}_5\text{CH}_3$	30	4.7	41 ^a
$\text{C}_6\text{H}_5\text{Cl}$	None	1290	None	64 ^b

^a 1.7% azobisisobutyronitrile.

^b 18% azobisisobutyronitrile.

The reaction is subject to catalysis by appropriate free radical sources. In Table XIII are gathered results using azobisisobutyronitrile at 80°C. The halides chosen are those which react slowly, if at all, at this temperature in the absence of a catalyst. There is no doubt that the azo compound exerts

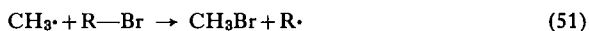
a profound catalytic effect. The presence of about 1.7 mole % of azobisisobutyronitrile in the reaction mixture results in substantial reaction in one-half hour, which is of the order of magnitude of the half-life of its decomposition, and implies a chain length greater than 100 in the cases of benzyl chloride, chlorocyclohexane, and bromobenzene. With chlorobenzene 18 mole-% of catalyst brought about 64% reduction in 21.5 hours; however, no reaction occurs at the reflux temperature even with the more reactive triphenyltin hydride in the absence of the catalyst (77). The chain length in this case must be quite short, implying that reaction (43) is relatively slow compared with chain termination steps.

TABLE XIV
RELATIVE RATES OF REDUCTION OF HALIDES BY TRI-*n*-BUTYLTIN HYDRIDE

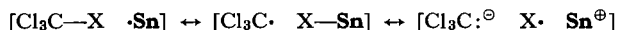
Halide	Rel. rate	Halide	Rel. rate
<i>At 45°C</i>			
C ₆ H ₅ CH ₂ Cl	0.05	CH ₂ =CHCH ₂ Br	31
<i>n</i> -C ₄ H ₉ Br	1.00	C ₆ H ₅ CH ₂ Br	34
1-BrC ₈ H ₁₇	1.10	BrCH ₂ CO ₂ C ₂ H ₅	50
Cyclo-C ₆ H ₁₁ Br	1.46	1-IC ₇ H ₁₅	61
Cyclo-C ₅ H ₉ Br	2.37	CCl ₄	76
2-BrC ₈ H ₁₇	2.63	BrCHCl ₂	112
2-BrC ₄ H ₉	2.99	HC≡CCH ₂ Br	139
<i>t</i> -C ₄ H ₉ Br	7.0	BrCCl ₃	226
BrCH ₂ Cl	26		
<i>At 80 ± 2°C</i>			
C ₆ H ₅ CH ₂ Cl	1	HC≡C—CH ₂ Cl	6.1
C ₆ H ₅ Br	0.72	2-BrC ₈ H ₁₅	30
CH ₂ =CHCH ₂ Cl	1.8	2-BrC ₄ H ₉	34

Another criterion of mechanism is the effect of structure on rate. It is reasonable to assume that the slowest step in the reaction chain is the abstraction of halogen atom from the halide, Eq. (43). Menapace has studied the relative reactivities of a number of halides by allowing them to compete in pairs for an insufficient amount of hydride and analyzing the resulting reaction mixture for unreacted starting materials, products, or both (32, 56). Pertinent results are listed in Table XIV. It is clear that the relative reactivities are those expected for a reaction leading to the production of a free radical. For example, benzyl bromide is more reactive than *t*-butyl bromide

by a factor of about 5, whereas *t*-butyl chloride solvolyzes faster than benzyl chloride by a factor which is strongly dependent upon the solvent (79). The sequence, $\text{BrCCl}_3 > \text{BrCHCl}_2 > \text{BrCH}_2\text{C}_6\text{H}_5 > \text{BrCH}_2\text{Cl}$, is the same as that found by Szwarc *et al.*, for the abstraction of bromine atoms by methyl radicals, Eq. (51) (80), although the range is considerably smaller in the

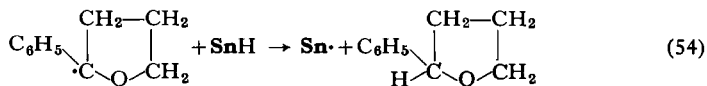
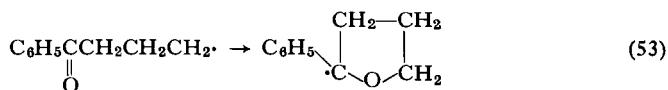
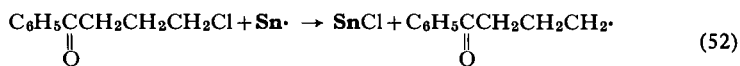


present case. Benzyl bromide is more reactive than the chloride by a factor of 680, but 1-bromotrichloromethane is more reactive than carbon tetrachloride by only a factor of about 3. 1-Iodoheptane is only about 60 times as reactive as the *n*-alkyl bromides. Quite surprising also is the fact that the *s*-alkyl bromides are only about 45 times as reactive as bromobenzene. Although an attempt at a detailed analysis of these relative reactivities would be premature, it is very probable that the energies of the carbon-halogen bonds as well as polar factors play important roles. The latter may be particularly important in the case of the polyhalomethanes in which the transition states may have important contributions from structures such as the following:

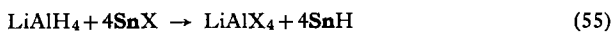


This reaction promises to be a useful one for studies on polar effects involving the relatively electropositive tin radicals as a complement to work which has already been done on the electronegative radicals such as *t*-butoxy and chlorine atoms.

As will be discussed in Section E, aldehydes and ketones are good traps for acyl radicals. Attempts to trap the alkyl radicals, postulated as intermediates in the alkyl halide reduction, by added ketone or aldehyde were unsuccessful. (Carbonyl reduction was not observed.) But reduction of 4-chlorobutyrophenone provided as the major product, 2-phenyltetrahydrofuran, whose formation can be rationalized according to Eqs. (52-54).



A promising simple method for the reduction of certain halides has been developed (32a). It takes advantage of the following facts: Lithium aluminum hydride reacts with organotin halides very rapidly; it reacts slowly by a nucleophilic displacement mechanism with halides; organotin hydrides react with halides by a free radical mechanism. This suggests the use of an organotin halide as a "hydride carrier" for the reduction of organic halides by lithium aluminum hydride. The reaction sequence is given by Eqs. (55),



(56). A few mole per cent of the organotin halide is added to a solution containing a mole of organic halide and an equivalent of lithium aluminum hydride. The organotin hydride is generated in reaction (55), it reduces the organic halide in reaction (56), thus regenerating organotin halide, which is then reduced with more lithium aluminum hydride. This method has been applied to the reduction of bromocyclohexane and used as a method for determining the relative abilities of several organotin hydrides as reducing agents. The results, shown in Table XV, lead to an order of effectiveness of the hydrides as follows: $(\text{C}_6\text{H}_5)_2\text{SnH}_2 \cong \text{C}_4\text{H}_9\text{SnH}_3 > (\text{C}_6\text{H}_5)_3\text{SnH} \cong (n\text{-C}_4\text{H}_9)_2\text{SnH}_2 > (n\text{-C}_4\text{H}_9)_3\text{SnH}$. Phenyltin trihydride and tin hydride were found to undergo decomposition too rapidly to be effective reducing agents.

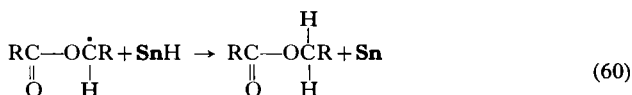
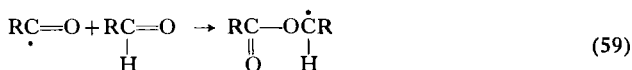
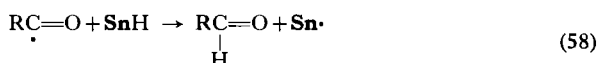
TABLE XV
REDUCTION OF BROMOCYCLOHEXANE BY ORGANOTIN HYDRIDES
GENERATED *in situ* BY LITHIUM ALUMINUM HYDRIDE^a

Organotin halide	Reaction time (min)	% Reduction
None	2645	1.4
$(\text{C}_6\text{H}_5)_3\text{SnCl}$	30	18
	150	80
$(n\text{-C}_4\text{H}_9)_3\text{SnCl}$	45	1.0
	1610	47
$(\text{C}_6\text{H}_5)_2\text{SnCl}_2$	30	22
	110	89
$(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$	40	7.0
	780	80
$n\text{-C}_4\text{H}_9\text{SnCl}_3$	35	22
	90	99

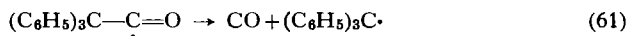
^a In refluxing diethyl ether; 2.5 mole % of organotin halide used; bromocyclohexane 1.2 M.

E. Reduction of Acyl Halides

Acid chlorides are reduced by organotin monohydrides as easily as aliphatic bromides. Benzaldehyde is reduced by triphenyltin hydride (48) and tri-*n*-butyltin hydride (32). Inasmuch as aldehydes are reduced quite slowly by the monohydrides this reaction would appear to constitute a convenient method for their synthesis from acid chlorides. However, the reaction product mixture invariably contains ester as well as aldehyde. In the case of benzoyl chloride, for example, reduction with tri-*n*-butyltin hydride in ether provided benzaldehyde (54%) as the major reduction product; in the absence of solvent benzyl benzoate (58%) predominated. The reaction sequence (57–60) has been postulated to account for the products formed (32).



Several observations indicate that this is reasonable. When a mixture of benzaldehyde and *iso*-butyryl chloride is treated with the organotin hydride, benzyl *iso*-butyrate is formed, but *iso*-butyl benzoate is not. Similarly when a mixture of benzoyl chloride and *iso*-butyraldehyde is reduced *iso*-butyl benzoate is formed, but benzyl *iso*-butyrate is not. Ethyl chloroformate is reduced very slowly at 80° C by tri-*n*-butyltin hydride, but the addition of 2 mole-% of azobisisobutyronitrile leads to facile reduction. When triphenylacetyl chloride is reduced at 100° C with the same hydride the products include triphenylacetaldehyde, triphenylmethane, and carbon monoxide, but little, if any, β,β,β -triphenylethyl triphenylacetate. The formation of carbon monoxide and triphenylmethane can be attributed to decarbonylation of the intermediate acyl radical to the more stable trityl radical, Eq. (61), which subsequently abstracts a hydrogen atom from the



tin hydride. An alternative course involving the decarbonylation of the triphenylacetyl chloride, catalyzed by the tri-*n*-butyltin chloride, followed by

reduction of the resulting trityl chloride, has been shown by Walsh (32) not to occur.

The synthetic utility of this reaction may be limited because both ester and aldehyde are formed. Nevertheless, some control of the product distribution appears to be possible because use of a solvent causes a marked increase in the yield of aldehyde. The reaction sequence (59–60) constitutes a reductive acylation of the aldehyde. A number of added aldehydes and ketones have been found to function in this manner. This provides a means of comparing the relative efficiencies of such compounds as traps for the acyl radicals. Apparently the polar factor is an important one in this case since the carbonyl compound competes effectively with the tin hydride for the acyl radical, whereas this is not the case for the alkyl radicals which are intermediates in reductions of alkyl halides.

F. Reaction with Carboxylic Acids

The normal reaction of organotin hydrides with mineral acids results in the formation of hydrogen and the organotin salt. The dihydrides, however, can give different products depending on the acid used and the organic

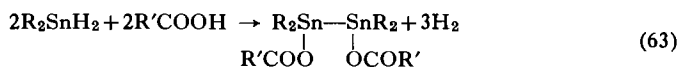
TABLE XVI
REACTIONS OF DIPHENYLTIN DIHYDRIDE WITH RCOOH TO FORM
1,1,2,2-TETRAPHENYL-1,2-DIACYLOXYDITINS

RCOOH	Ratio of acid to hydride	Yield (%)	Moles H ₂ /mole (C ₆ H ₅) ₂ SnH ₂	M.p. (°C)
Acetic	0.8	75	1.22 ^a	152
Monochloroacetic	0.8	83	1.57 ^a	150
	2.0	35	1.31	150
Dichloroacetic	0.8	75	1.37 ^a	169
Trichloroacetic	2.0	35	0.55 ^b	170
Trifluoroacetic	2.5	32	0.96	165
Benzoic	1.5	68	1.52	185
<i>o</i> -Chlorobenzoic	1.5	47	1.69	161
<i>o</i> -Hydroxybenzoic	2.0	32	1.29	197
Hexanoic	2.0	49	1.52	85–87
Octanoic	2.0	7	1.48	86–88

^a Moles of H₂/mole of acid since hydride was in excess.

^b Test showed no unused hydride.

groups on the tin atom (26–28). Treatment of diphenyltin dihydride with carboxylic acids leads to the formation in good yields of 1,1,2,2-tetraphenyl-1,2-diacyloxyditins, Eq. (63), rather than the diphenyltin dicarboxylates,



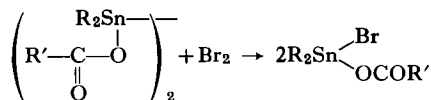
Eq. (62). Results are listed in Table XVI. The formation of fewer than 1.5 moles of hydrogen/mole of hydride indicates that the lower yields are

TABLE XVII
REACTIONS OF DI-*n*-BUTYLtin DIHYDRIDE WITH RCOOH
TO FORM $\text{Bu}_2\text{Sn}(\text{OCOR})_2(\text{A})$ AND $(\text{Bu}_2\text{SnOCOR})_2(\text{B})$

RCOOH	Ratio of acid to hydride	Type of product	Yield of product ^a (%)	% B ^b	Moles H ₂ /mole Bu ₂ SnH ₂	M.p. ^c (°C)
Acetic	2.0	A	90	—	1.98	8.5–10
	1.14	B	65	68	1.57	–7.0 to –4.0
Monochloroacetic	2.0	A	80.5	Trace	1.94	87–89
Dichloroacetic	2.0	A	16	—	1.98	112–114
Trichloroacetic	2.0	— ^d	— ^d	—	1.13	— ^d
Trifluoroacetic	2.0	A	— ^d	Trace	1.99	— ^d
Benzoic	2.0	A	52	9	1.63	68–71
	1.0	B	65	69	1.41	31.5–32.5
<i>o</i> -Chlorobenzoic	0.76	B	60	—	1.78 ^e	65–66.5
<i>p</i> -Chlorobenzoic	0.80	B	15.5	—	1.69 ^e	75–77
Succinic	0.83	A	71	0	— ^f	185.5–187.5
Lauric	0.77	B ^g	96 ^d	—	1.66	— ^g

^a Of sample purified for analysis.

^b In product mixture as determined by bromine analysis:



^c Taken by normal method.

^d Analytically pure product not isolated.

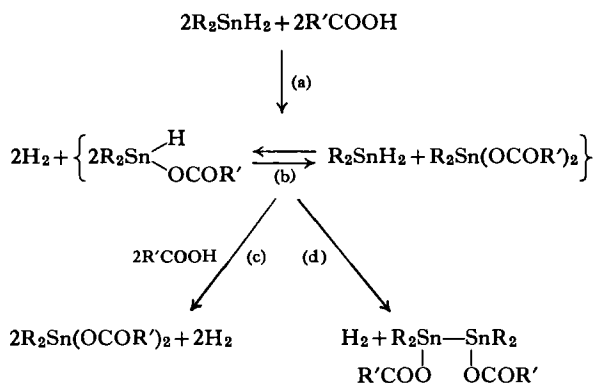
^e Moles of H₂/mole of acid since hydride was in excess.

^f Not measured.

^g Product not isolated but measured by bromine titration.

not due to the incursion of reaction (62), which requires formation of 2 moles of hydrogen/mole of hydride. The lower yields obtained from the haloacetic acids are undoubtedly due to consumption of hydride in reduction of the halomethyl groups as an important side reaction. Fair to good yields of either simple dicarboxylate or ditin dicarboxylate can be obtained with di-*n*-butyltin dihydride, depending on the ratio of acid to hydride used, as is shown in Table XVII. Succinic acid is an exception, giving the tetrameric succinate even when a low ratio of acid to hydride is used.

The formation of the products observed can be rationalized in terms of the set of reactions, shown in the chart, which has been suggested by the results



of a detailed study of the reaction between di-*n*-butyltin dihydride and acetic acid (28). Reaction (a) has been shown to occur by the addition of one mole of acid to one mole of the hydride. The equilibrium (b) can be established by simply mixing the dihydride and the dicarboxylate. If this equilibrium mixture is allowed to stand, slow hydrogen evolution ensues and the ditin dicarboxylate is formed according to reaction (d); if a mole of acid is added, reaction (c) ensues and the simple dicarboxylate results. When diphenyltin dihydride is used the intermediate diphenylacyloxytin hydride decomposes so rapidly that reaction (c) does not compete effectively.

The formation of 1,1,2,2-tetraphenyldiaclyoxyditins has also been observed in the reaction of triphenyltin hydride with benzoic, 2-thenoic, and furoic acids. The latter two acids also gave the simple triphenyltin carboxylates, whereas acetic and propionic acids gave only the simple carboxylates (81). How the ditin compounds come about in these cases remains to be ascertained.

G. Other Reactions

The reduction of alkyl, aryl, and acyl halides by organotin hydrides would suggest that other halides might also be reduced. It has been shown that *N*-bromosuccinimide is reduced in 95% yield with triphenyltin hydride (82). Diphenylchlorophosphine undergoes exothermic reduction with triphenyltin hydride providing diphenylphosphine in good yield (83).

Lesbre and Buisson have shown that tri-*n*-propyltin hydride reacts with aliphatic azo compounds in the presence of copper powder to give insertion products according to Eq. (64) (84). Among the groups which have been



inserted into this organotin hydride are $\text{CHCOOC}_2\text{H}_5$, CHCOCH_3 , CHCOC_6H_5 . Tri-*n*-butyltin hydride reacted with diazoacetone nitrile to produce cyanomethyltri-*n*-butyltin.

REFERENCES

1. F. Paneth and K. Furth, *Ber. Deut. Botan. Ges.* **52**, 2020 (1919).
2. W. Vaubel, *Ber. Deut. Botan. Ges.* **57B**, 515 (1924).
3. F. Paneth, W. Haken, and E. Rabinowitsch, *Ber. Deut. Botan. Ges.* **57B**, 1891 (1924).
4. F. Paneth, A. Johannsen, and M. Matthies, *Ber. Deut. Botan. Ges.* **55**, 769 (1922).
5. E. J. Weeks, *Rec. Trav. Chim.* **45**, 201 (1926).
6. G. W. Schaeffer and Sister M. Emilius, *J. Am. Chem. Soc.* **76**, 1203 (1954).
7. V. M. Vdovenko, *Compt. Rend. Acad. Sci. URSS* **23**, 801 (1939); *Chem. Abstr.* **34**, 3601 (1940).
8. I. P. Alimarin and P. E. Arest-Yakubovich, *J. Appl. Chem. (USSR)* **10**, 920 (1937); *Chem. Abstr.* **31**, 6573 (1937).
9. A. F. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. J. Schlesinger, *J. Am. Chem. Soc.* **69**, 2692 (1947).
10. K. Tamaru, *J. Phys. Chem.* **60**, 610 (1956).
11. L. May and C. R. Dillard, *J. Chem. Phys.* **34**, 694 (1961).
12. H. J. Emel us and S. F. A. Kettle, *J. Chem. Soc.* p. 2444 (1958).
13. D. R. Lide, Jr., *J. Chem. Phys.* **19**, 1605 (1951).
14. R. Mathis-Noel, M. Lesbre, and I. Seree de Roch, *Compt. Rend.* **243**, 257 (1956).
15. C. R. Dillard, E. H. McNeill, D. E. Simmons, and J. B. Yeldel, *J. Am. Chem. Soc.* **80**, 3607 (1958).
16. G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* **7**, 366 (1957).
17. W. J. Considine and J. J. Ventura, *Chem. Ind. (London)* p. 1683 (1962).
18. W. P. Neumann, *Angew. Chem.* **73**, 542 (1961).
19. W. P. Neumann and H. Niermann, *Ann. Chem.* **653**, 164 (1962).
20. W. P. Neumann, H. Niermann, and R. Sommer, *Angew. Chem.* **73**, 768 (1961).
- 20a. W. P. Neumann and E. Heymann, *Angew. Chem.* **75**, 166 (1963).
- 20b. R. Calas, J. Valade, and J. C. Pommier, *Compt. Rend.* **255**, 1450 (1962).

- 20c. J. Valade and J. C. Pommier, *Bull. Soc. Chim. France* p. 199 (1963).
- 20d. G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.* **84**, 208 (1962).
21. W. P. Neumann, H. Niemann, and R. Somer, *Ann. Chem.* **659**, 27 (1962).
22. G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *Chem. Ind. (London)* p. 1290 (1958).
23. C. A. Kraus and W. N. Greer, *J. Am. Chem. Soc.* **44**, 4269 (1922).
24. R. F. Chambers and P. C. Sherer, *J. Am. Chem. Soc.* **48**, 1054 (1926).
25. E. Amberger, *Angew. Chem.* **72**, 78 (1960).
26. A. K. Sawyer and H. G. Kuivila, *J. Am. Chem. Soc.* **82**, 5958 (1960).
27. A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.* **27**, 610 (1962).
28. A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.* **27**, 837 (1962).
29. A. K. Sawyer and H. G. Kuivila, *Chem. Ind. (London)* p. 260 (1961).
30. W. L. Jolly, *Angew. Chem.* **27**, 268 (1960).
31. W. L. Jolly, *J. Am. Chem. Soc.* **83**, 335 (1961).
32. E. J. Walsh, unpublished observation from the author's laboratory.
- 32a. H. G. Kuivila and L. W. Menapace, *J. Org. Chem.* **28**, 2165 (1963).
33. W. P. Neumann and K. Konig, *Angew. Chem.* **74**, 215 (1962).
34. W. P. Neumann, *Angew. Chem.* **74**, 122 (1962).
35. H. G. Kuivila, A. K. Sawyer, and A. G. Armour, *J. Org. Chem.* **26**, 1426 (1961).
36. S. F. A. Kettle, *J. Chem. Soc.* p. 2937 (1959).
37. J. G. Noltes and G. J. M. van der Kerk, *Rec. Trav. Chim.* **81**, 41 (1962).
38. A. Stern and E. I. Becker, *J. Org. Chem.* **27**, 4052 (1962).
39. G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *Rec. Trav. Chim.* **81**, 853 (1962).
40. A. B. Burg and J. R. Spielman, *J. Am. Chem. Soc.* **83**, 2667 (1961).
41. L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.* **69**, 188 (1947).
42. C. A. Burkhard and R. H. Kriebel, *J. Am. Chem. Soc.* **69**, 2687 (1947).
43. A. J. Barry, L. De Pree, J. W. Gilkey, and D. E. Hook, *J. Am. Chem. Soc.* **69**, 2916 (1947).
44. A. K. Fischer, R. C. West, and E. G. Rochow, *J. Am. Chem. Soc.* **76**, 5878 (1954).
45. H. Gilman and J. Eisch, *J. Org. Chem.* **20**, 763 (1955).
46. R. Fuchs and H. Gilman, *J. Org. Chem.* **22**, 1009 (1957).
47. G. J. M. van der Kerk, J. G. A. Luijten, and J. G. Noltes, *Chem. Ind. (London)* p. 352 (1956).
48. G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* **7**, 356 (1957).
49. G. J. M. van der Kerk and J. G. Noltes, *J. Appl. Chem.* **9**, 106 (1959).
50. M. C. Henry and J. G. Noltes, *J. Am. Chem. Soc.* **82**, 558 (1960).
51. G. J. M. van der Kerk, J. G. A. Luijten, and J. G. Noltes, *Angew. Chem.* **70**, 298 (1958).
52. G. J. M. van der Kerk and J. G. Noltes, *J. Appl. Chem.* **9**, 113 (1959).
53. G. J. M. van der Kerk and J. G. A. Luijten, *J. Appl. Chem.* **6**, 93 (1956).
54. J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," p. 25. Tin Research Institute, Greenford, England, 1956.
55. E. M. Smolin, *Tetrahedron Letters* p. 143 (1961).
56. H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.* **84**, 3584 (1962).
57. C. G. Krespan and V. A. Engelhardt, *J. Org. Chem.* **23**, 1565 (1958).
58. M. C. Henry and J. G. Noltes, *J. Am. Chem. Soc.* **82**, 56 (1960).
59. J. G. Noltes and G. J. M. van der Kerk, *Chimia (Aarau)* **16**, 122 (1962).
60. H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.* **80**, 3250 (1958).
61. J. G. Noltes and G. J. M. van der Kerk, *Rec. Trav. Chim.* **80**, 623 (1962).

62. R. F. Fulton, Ph.D. Dissertation, Purdue Univ., Lafayette, Indiana, 1960; *Dissertation Abstr.* **22**, 3397 (1962).
63. H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.* **80**, 3789 (1958).
64. H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.* **83**, 1246 (1961).
65. R. Calas and N. Duffaut, *Compt. Rend.* **245**, 306 (1957).
66. J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind. (London)* p. 294 (1959).
67. O. F. Beumel, Jr., Ph.D. Dissertation, Univ. New Hampshire, Durham, New Hampshire, 1960.
68. E. J. Eliel and R. S. Rao, *J. Am. Chem. Soc.* **79**, 5992 (1957).
69. A. K. Macbeth and J. S. Shannon, *J. Chem. Soc.* p. 2852 (1952).
70. R. H. Reitsema, *J. Am. Chem. Soc.* **75**, 1996 (1953).
71. J. Valade, M. Pereyre, and R. Calas, *Compt. Rend.* **253**, 1216 (1961).
72. A. K. Sawyer, private communication.
73. D. H. Lorenz and E. I. Becker, private communication.
74. D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.* **28**, 703 (1963).
75. E. J. Kupchik and R. J. Kiesel, *Chem. Ind. (London)* p. 1654 (1962).
76. D. H. Lorenz and E. I. Becker, *J. Org. Chem.* **27**, 3370 (1962).
77. L. A. Rothman and E. I. Becker, *J. Org. Chem.* **25**, 2203 (1960).
78. S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.* **80**, 635 (1958).
79. A. Streitwieser, Jr., *Chem. Rev.* **56**, 616 (1956).
80. F. W. Evans, R. J. Fox, and M. Szwarc, *J. Am. Chem. Soc.* **82**, 6414 (1960).
81. S. Weber and E. I. Becker, *J. Org. Chem.* **27**, 1258 (1962).
82. E. J. Kupchik and T. Lanigan, *J. Org. Chem.* **27**, 3661 (1962).
83. D. Seyferth and M. Takamizawa, private communication.
84. M. Lesbre and R. Buisson, *Bull. Soc. Chim. France* p. 1204 (1957).

Organic Substituted Cyclosilanes*

HENRY GILMAN and GERALD L. SCHWEBKE

Iowa State University, Ames, Iowa

I. Introduction	90
A. Bonding to Silicon	90
B. Polysilanes	90
C. Catenation of Group IVb Elements	90
D. Cyclosilanes	91
II. Nomenclature	93
III. Structure and Properties of the Cyclosilanes	94
A. Physical Properties and Structure Determination	94
B. Reactivity of the Si-Si Bond	105
C. Ring Strain	107
IV. Formation of the Cyclosilanes	110
A. From Dichloromonosilanes and Metals	110
B. By Cyclization of α,ω -Dihalopolysilanes with Metals	113
C. Other Cyclization and Conversion Reactions	114
V. General Reactions of the Cyclosilanes	115
A. Reactions with Lithium Metal	115
B. Halogenation Reactions	115
C. Reactions with Bases	116
D. Miscellaneous Reactions	116
VI. Reactions of Octaphenylcyclotetrasilane	117
A. With Lithium Metal	117
B. With Halogens and Hydrogen Halides	119
C. With Inorganic Halides and Metal Salts	120
D. With Organic Halides	120
E. With Organometallic and Organosilylmetallic Reagents	121
F. With Oxidizing Agents	123
G. With Hydrogen	124
VII. Reactions of Decaphenylcyclopentasilane	125
A. With Lithium Metal	125
B. With Halogens	127
C. With Other Halogenating Agents	129
D. With Organometallic and Organosilylmetallic Reagents	129
VIII. Reactions of Compound "C"	130
A. With Lithium Metal	130
B. With Halogens	132
C. With Organometallic Reagents	132

* In this contribution, literature references and explanatory notes are cited by superscript arabic numerals.

IX. Reactions of Dodecamethylcyclohexasilane	132
A. With Halogenating Agents	132
B. With Organometallic Reagents	133
X. Organopolysilanes	133
XI. Summary and Conclusions	136
References	137

I

INTRODUCTION

A. Bonding to Silicon

Silicon, in its compounds, forms bonds of a covalent nature and is, with limitations, similar to saturated carbon. However, because silicon is decidedly more electropositive than carbon, its bonding to other elements has more ionic character and, therefore, is subject to a greater ease of heterolytic fission by polar reagents. Also, the available *d* orbitals of silicon probably play an important role in many reactions at silicon.¹

B. Polysilanes

One property shared by both carbon and silicon is the ability to form stable covalent atom-to-atom bonds, i.e. $\equiv\text{C}-\text{C}\equiv$ and $\equiv\text{Si}-\text{Si}\equiv$. The catenation of carbon is well known and is exemplified in its straight-chain paraffinic compounds. The first four members of the analogous series of silanes ($\text{Si}_n\text{H}_{2n+2}$), prepared by the acid hydrolysis of magnesium silicide, were initially characterized by Stock² and co-workers. With the advent of gas chromatography, such hydrolysis mixtures were shown to contain at least twenty-one components, with polysilanes of chain lengths as long as eight silicon atoms being tentatively identified.³ Chlorine-substituted polysilanes and their corresponding hydrolysis products with chain lengths of ten silicon atoms have been characterized.⁴ Although the polysilanes appear to be less stable than their carbon counterparts,⁵ they are certainly sufficiently stable to make their isolation and characterization possible.

C. Catenation of Group IVb Elements

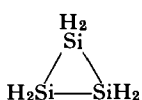
Organic substituted polysilanes are known and will be discussed at a later place in the chapter. Other elements of Group IVb have a tendency toward

catenation, and organic derivatives of polygermanes and polystannanes of chain lengths up to six or seven are known.^{6a-6c} The tendency toward catenation decreases in going from silicon to lead, and no organolead compounds are known with more than two lead atoms bound together in a chain.^{6a}

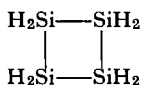
Recently, the structure and chemistry of materials of the type $(\text{SiH}_2)_n$ and $(\text{SiH})_n$ have been investigated and reviewed.⁷ However, these compounds cannot be considered analogous to the alkene or alkyne series in carbon chemistry because of their polymeric nature. The inability of silicon to form multiple bonds with itself or other elements is well known, but perhaps not easily explained.⁸ It might be pointed out that none of the elements below the second period in the periodic table appears to form stable double bonds with themselves. For example, the compounds "phosphobenzene" and "arsenobenzene," supposedly analogs of azobenzene, are better described as tetraphenylcyclotetraphosphine⁹ and hexaphenylcyclohexaarsine,¹⁰ respectively. Also, sulfur, under ordinary conditions, exists as a cyclic octamer.

D. Cyclosilanes

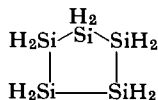
A class of polysilanes which can be envisioned as analogous to the cycloalkanes is the cyclosilanes, of which cyclotrisilane (1), cyclotetrasilane (2), cyclopentasilane (3), and cyclohexasilane (4) would be examples. Although existence of these simple cyclosilanes has not been documented in the



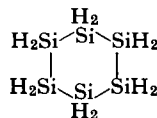
(1)



(2)



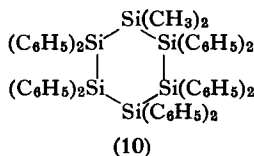
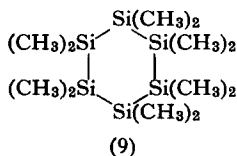
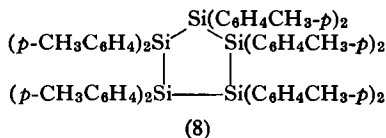
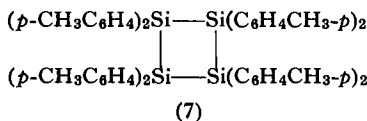
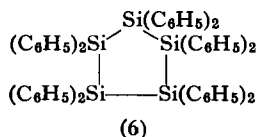
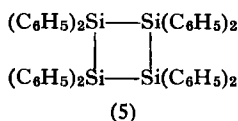
(3)



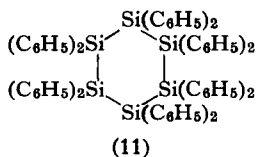
(4)

literature to date, they cannot be ruled out as minor products or possible intermediates in the acid hydrolysis of magnesium silicide.^{2,3} Attempts to prepare compounds of the silylene type, $(\text{SiH}_2)_n$, either by hydrolysis of the calcium silicide, CaSi ,¹¹ or by reaction of dichlorosilane with sodium amalgam,¹² resulted in the isolation of polymeric materials with less than the required stoichiometric amount of hydrogen. The fact that the simple cyclosilanes are unknown may very well be due not to the lack of stability of these compounds, but to the lack of synthetic methods.

However, cyclosilanes which are completely substituted with organic groups are known.^{13-19a} These compounds conform to the general formula $(\text{SiR}_2)_n$, consisting of a cycle of n silicon atoms, each of which bears two organic groups. At present, the known organic substituted cyclosilanes consist of four-, five-, or six-membered rings, which are substituted by phenyl, *p*-tolyl, or methyl groups. Thus, compounds (5-10) have been prepared and their structures have been elucidated either by direct examination or by analogy to the phenylated series (5-6). Also, in the phenylated series a third compound of undetermined structure is known.



It may possibly be the next member (11) in the homologous series.



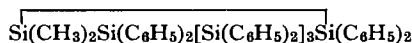
The purpose of this chapter is to discuss the structure, properties, preparation, and reactions of the cyclosilanes in the light of recent investigations of the phenyl and methyl series, and to correct some misconceptions concerning the perphenylated cyclosilanes. Because reactions of these cyclosilanes invariably lead to polysilanes, a section has been included to list these derivatives, many of them new compounds, in tabular form.

II

NOMENCLATURE

In naming organosilicon compounds having silicon chains, the rules of nomenclature recommended by the Commission of Nomenclature of Organic Chemistry of the I.U.P.A.C.,²⁰ and adopted by the American Chemical Society,²¹ will be used with the exceptions noted below. Organosilicon compounds having open silicon atom chains will be named as derivatives of compounds of the general formula $\text{H}_3\text{Si}(\text{SiH}_2)_n\text{SiH}_3$ and will be called disilanes, trisilanes, tetrasilanes, etc. The generic name of such compounds is *silanes*. For designating the position of substituents in compounds named as silanes, each member will be numbered from one terminal silicon atom to the other. Because the compounds discussed here are highly substituted straight-chain silanes bearing generally the same organic substituents of each silicon atom, with varying terminal groups, the position of these organic substituents will not be numbered in order to avoid unwieldy sequences of numbers. Therefore, the compound of the formula $\text{BrSi}(\text{C}_6\text{H}_5)_2[\text{Si}(\text{C}_6\text{H}_5)_2]_3\text{Si}(\text{C}_6\text{H}_5)_2\text{Br}$ will be named 1,5-dibromodecaphenylpentasilane, instead of 1,5-dibromo-1,1,2,2,3,3,4,4,5,5-decaphenylpentasilane. The numbering of the phenyl groups is unnecessary, as the shorter name is unambiguous. Also, again to avoid long series of numbers for silane derivatives containing the Si—H group, the naming is accomplished by prefixing to the rest of the name a position symbol, followed by italic capital *H*, for each such group. Thus, $\text{HSi}(\text{C}_6\text{H}_5)_2[\text{Si}(\text{C}_6\text{H}_5)_2]_5\text{Si}(\text{C}_6\text{H}_5)_2\text{H}$ will be named 1*H*, 7*H*-tetradecaphenylheptasilane, and $\text{HSi}(\text{C}_6\text{H}_5)_2[\text{Si}(\text{C}_6\text{H}_5)_2]_2\text{Si}(\text{C}_6\text{H}_5)_2\text{OH}$ will be 4*H*-octaphenyltetrasilane-1-ol.

Organosilicon compounds containing chains of silicon atoms in a cycle will be named as derivatives of cyclic silicon compounds having the formula $(\text{SiH}_2)_n$ and will be called cyclotrisilanes, cyclotetrasilanes, etc., according to the number of members in the ring; they will have the generic name *cyclosilanes*. Cyclosilanes will be numbered in the same way as are carbon compounds of a similar nature. Therefore, the compound



will be named 1,1-dimethyldecaphenylcyclohexasilane.

Other groups and radicals which are substituents will be named as they are in carbon chemistry. For example, $n\text{-C}_3\text{H}_7\text{OSi}(\text{C}_6\text{H}_5)_2[\text{Si}(\text{C}_6\text{H}_5)_2]_3\text{Si}(\text{C}_6\text{H}_5)_2\text{OC}_3\text{H}_7$ -*n* will be named 1,5-di-*n*-propoxydecaphenylpentasilane.

Where such naming, as outlined above, might be ambiguous, the full name with all substituents assigned a number will be used.

III

STRUCTURE AND PROPERTIES OF THE CYCLOSILANES

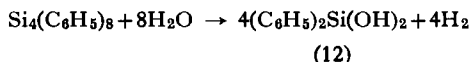
A. Physical Properties and Structure Determination

Organic substituted cyclosilanes were first recognized as products of reactions designed to prepare compounds containing silicon-silicon double bonds. It would appear that the first substituted cyclosilane or possible mixture of cyclosilanes was prepared by F. S. Kipping by the reaction of dichloroethylphenylsilane with sodium to give a material described as "diphenyldiethylsilicoethylene."²² Only a few properties of this substance were given. It was described as a vitreous, easily fusible solid which was soluble in common organic solvents except alcohols. Although this material was not recognized as such, it may have been a cyclosilane because the reaction of dichlorosilanes with alkali metals has since been recognized as resulting in cyclosilanes, and because of the fact that silicon is not known to form stable double bonds with another silicon atom, as carbon does with itself in ethylene compounds.

The first examples of well-defined cyclosilanes, also reported by Kipping, were products obtained from the reaction of sodium with dichlorodiphenylsilane in boiling toluene.¹³ Three distinct crystalline compounds were isolated; they were designated as Compound "A,"¹³ Compound "B,"¹³ and Compound "C."¹⁴ Other amorphous solids¹⁴ and intractable glues²³ were also obtained, although now they appear to have been polymeric in nature. Compound "A" was also prepared in comparable yield from chlorophenoxydiphenylsilane and sodium.²⁴

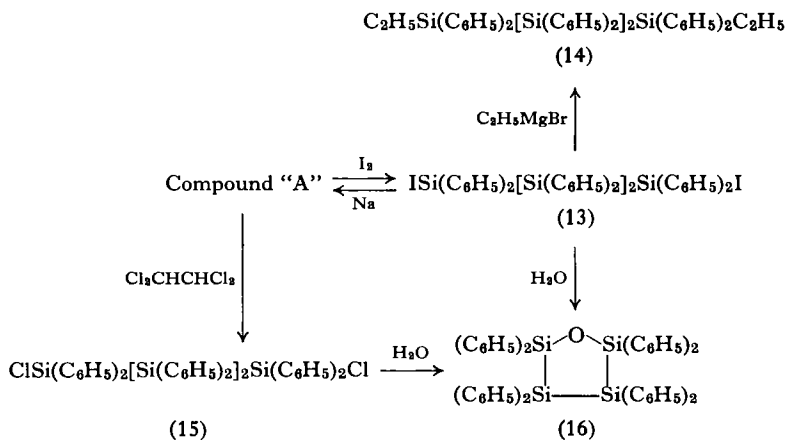
The determination of the structures of Compound "A" and Compound "B" presented a very interesting problem, which has been resolved only recently. Inaccurate data obtained for the molecular weight of Compound "B" led to a difficulty concerning the relationship of the two compounds. Both materials were shown by elemental analysis and hydrogen value determinations^{25,26} to be of the general formula $[\text{Si}(\text{C}_6\text{H}_5)_2]_n$.¹³ Also, both compounds upon hydrolysis with aqueous piperidine gave only diphenylsilanediol (12), or its siloxane condensation products. The disturbing fact

was that molecular weight determinations appeared to indicate that the two compounds were isomers of the formula $[\text{Si}(\text{C}_6\text{H}_5)_2]_4$.

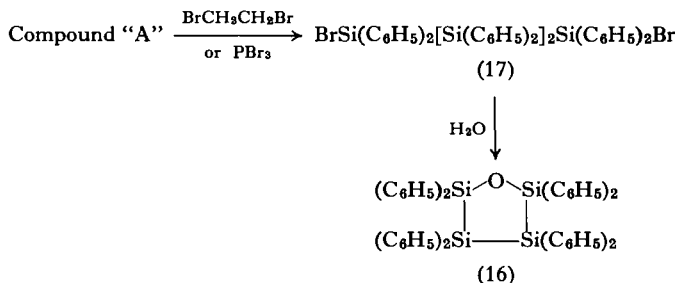


The molecular weights obtained for Compound "A" were 637 and 699, while those for Compound "B" were recorded as 734, 718, and 718.¹³ Both were determined cryoscopically in benzene, with molecular weights for the former compound being more suspect due to its low solubility in benzene. The calculated molecular weight for $\text{Si}_4(\text{C}_6\text{H}_5)_8$ is 729, while those for the next lower and next higher homologs are 547 and 911, respectively. Although the observed molecular weight for Compound "B" corresponded closely to that expected for a tetrasilane, Kipping was unable to obtain any characteristic derivatives of it due to its stability to the reagents which were tried.^{13, 14}

On the other hand, Compound "A," melting at *ca.* 335° C, was characterized by its extreme reactivity in comparison to "B," resulting in derivatives which indicated very definitely that "A" was a tetrasilane. Thus, Compound "A" readily reacted with iodine to give 1,4-diiodooctaphenyltetrasilane (13), which could be reconverted to "A" by sodium in refluxing toluene.¹³ The diiodo derivative could also be converted to 1,4-diethyloctaphenyltetrasilane (14) by means of ethylmagnesium bromide.²⁷ Phenylmagnesium bromide did not react similarly, and this was attributed to steric factors. Compound "A" also reacted with *sym*-tetrachloroethane to give 1,4-dichlorooctaphenyltetrasilane (15), which was shown to be analogous



to the diiodo derivative by conversion to the common hydrolysis product, octaphenyloxacyclopentasilane (16).¹³ Refluxing with 1,2-dibromoethane or phosphorus tribromide transformed "A" into 1,4-dibromooctaphenyltetrasilane (17), which was not isolated but converted directly to the cyclic oxide (16) by aqueous acetone.²⁸ Compound "A" was decomposed readily with oxygenating agents, such as refluxing nitrobenzene,¹³ benzaldehyde and amyl nitrite,²⁸ as well as oxygen and ozone, to give several oxygenated products in varying amounts.²⁸ Compound "B," a material of rather greater solubility than "A" and not melting below 360° C, was found to be generally unreactive with all these reagents under similar conditions.

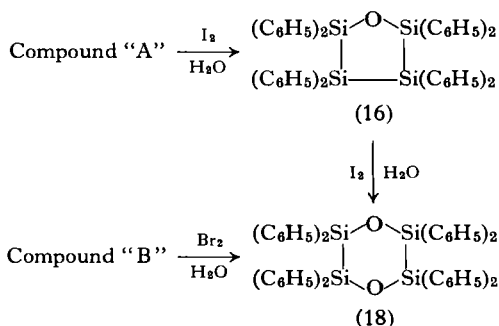


Kipping was then left with assigning a structure to the significantly different compounds, each of which appeared to be an octaphenyltetrasilane.

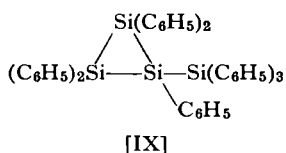
TABLE I
STRUCTURES CONSIDERED BY KIPPING FOR COMPOUND "A"¹³

[I]	$(\text{C}_6\text{H}_5)_2\text{Si}=\text{Si}(\text{C}_6\text{H}_5)_2$
[II]	$ \begin{array}{c} (\text{C}_6\text{H}_5)_2\text{Si}-\text{Si}(\text{C}_6\text{H}_5)_2 \\ \qquad \qquad \\ (\text{C}_6\text{H}_5)_2\text{Si}-\text{Si}(\text{C}_6\text{H}_5)_2 \end{array} $
[III]	$(\text{C}_6\text{H}_5)_3\text{SiSi}(\text{C}_6\text{H}_5)=\text{Si}(\text{C}_6\text{H}_5)-\text{Si}(\text{C}_6\text{H}_5)_3$
[IV]	$(\text{C}_6\text{H}_5)_3\text{SiSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)=\text{Si}(\text{C}_6\text{H}_5)_2$
[V]	$ \begin{array}{c} (\text{C}_6\text{H}_5)_3\text{Si} \diagdown \\ (\text{C}_6\text{H}_5)_3\text{Si} \diagup \text{Si}=\text{Si}(\text{C}_6\text{H}_5)_2 \end{array} $
[VI]	$\text{C}_6\text{H}_4=\text{Si}(\text{C}_6\text{H}_5)\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)=\text{C}_6\text{H}_4$
[VII]	$ \begin{array}{c} \text{C}_6\text{H}_4 \diagdown \\ \text{C}_6\text{H}_4 \diagup \text{SiSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagdown \\ \text{C}_6\text{H}_4 \end{array} \end{array} $
[VIII]	$\bullet\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\bullet$

Several possible structures were considered for Compound "A," which was termed by Kipping as "unsaturated."¹³



Structure [I] was quickly dismissed because of the reaction of "A" with iodine. While structure [II] was tenable for the "unsaturated" compound, this structure was reserved by him for Compound "B." A number of factors ruled against isomers [III, IV, and V], including the improbability of their formation in the reaction mixture producing "A," the fact that no triphenylsilanol was obtained from the hydrolysis of "A," and the fact that the same cyclic dioxide (18)²⁹ could be obtained starting with either "A" or "B."¹³ Hydrogen values, hydrolysis products, and behavior toward iodine eliminated isomers [VI] and [VII]. One other quite unlikely possibility for the structure of Compound "A" would be a cyclic conformation with a triphenylsilyl side chain [IX]. However, factors which rule against isomers [III, IV, and V], would also eliminate this configuration.



Kipping also suggested that the two compounds were possibly both octa-phenylcyclotetrasilane, one with all four silicons in a plane while, in the other, the silicons were in a tetrahedral arrangement.¹³ However, recognizing that its ready reaction with iodine and with oxidizing agents was reminiscent of the free radical species of carbon, Kipping assigned to Compound "A" an open-chain structure of four diphenylsilylene units with terminal tervalent silicon atoms, $\cdot\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\cdot$.²⁸ To Compound

"B," because of its relative stability to a variety of reagents, he assigned the closed-chain structure, octaphenylcyclotetrasilane (5).²⁸

Based on these conclusions, Compound "A" might be expected to be converted into Compound "B" simply by heating; however, it appeared to be stable to heat. When "A" was melted (about 335°C) in a sealed, exhausted tube, heated for 20 hours, and then allowed to cool, the pale yellow oil crystallized almost immediately and appeared to be unchanged "A."²⁸ In the work of Schlenk and Mark,³⁰ Kipping found support for a postulate that the structure of Compound "A," containing tervalent silicon, need not be prone to cyclize or polymerize. These workers had found that the free radical species, triphenylmethyl and pentaphenylethyl, did not combine to give octaphenylpropane, nor did pentaphenylethyl dimerize to produce deca-phenylbutane.

Six years later Kipping had occasion to publish results of the reaction of dichlorodi-*p*-tolylsilane with sodium in refluxing toluene,¹⁵ which gave a mixture of products, two of which were recognized as being analogous to compounds "A" and "B."³¹ Therefore, to the less soluble compound, melting at 290–293°C (dec.), Kipping assigned the structure of octa-*p*-tolyltetrasilane, with two tervalent silicon atoms. This material readily reacted with iodine to give 1,4-diiodoocta-*p*-tolyltetrasilane, which was in turn hydrolyzed to octa-*p*-tolylloxacyclopentasilane. It also underwent other reactions characteristic of Compound "A." The second compound, designated as octa-*p*-tolylcyclotetrasilane, by analogy to Compound "B," was found not to react with iodine, *sym*-tetrachloroethane, or nitrobenzene.

In 1937, when Kipping summarized his work in the field of organosilicon chemistry,³² he still considered the structures which he had assigned to Compounds "A" and "B" and their *p*-tolyl analogs to be correct. In view of the evidence which had been accumulated, these conclusions were justifiable.

The problem lay dormant until 1960, when, in connection with a study of the direct preparation of organosilyllithium compounds from chlorosilanes,³³ it was found that appreciable quantities of 1,4-dilithiooctaphenyltetrasilane were produced when an excess of lithium was allowed to react with dichlorodiphenylsilane in tetrahydrofuran.³⁴ It was also recognized that a compound identical with Kipping's Compound "A" was an intermediate in the reaction. An investigation of this material was undertaken, and electron paramagnetic resonance studies failed to detect unpaired electrons.³⁵ The structure therefore assigned to Kipping's Compound "A"

is octaphenylcyclotetrasilane (5), and its high reactivity is explained as due to ring strain in the cyclic structure.³⁵ Subsequently, it was discovered that the silicon-silicon bond in octaphenylcyclotetrasilane would react with a variety of halogenating agents, both organic and inorganic; with organolithium and organosilyllithium reagents; and with hydrogen chloride, hydrogen bromide, and hydrogen iodide. It might be pointed out that the reactivity of the silicon-silicon bond in octaphenylcyclotetrasilane is qualitatively of the order of that found in the unstrained systems of hexaphenylditin and hexaphenyldilead,^{6a, 6b} which react with halogens, alkali metals, and oxidizing agents. Hexaethylditin and hexaethyldilead have both been shown to react with 1,2-dibromoethane,³⁶ as does Compound "A."

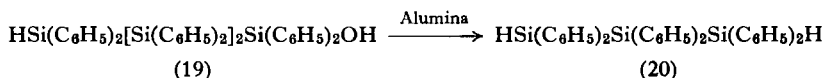
This then leaves the problem of the structure for Compound "B," which Kipping considered to be the cyclic tetramer.

As implied previously, Kipping had obtained inaccurate data which forced him into the position concerning Compound "A" outlined above. This concerned the molecular weight of Compound "B," the only evidence Kipping possessed which indicated that the compound was a tetrasilane. He had little chemical evidence for this assumption. The molecular weight did, in fact, appear to be a point of concern, because it was redetermined by him cryoscopically in both benzene and camphor,¹⁴ but again a tetrasilane was indicated. Kipping, however, did point out that experimentally determined molecular weights of hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane were 15 to 20% low in benzene.³⁷ Evidently Kipping did not follow this implication because the deviation of the molecular weight from a tetrasilane was not very great, and because he assumed that a difference in ring size would not explain sufficiently the great difference in reactivity of the two compounds.

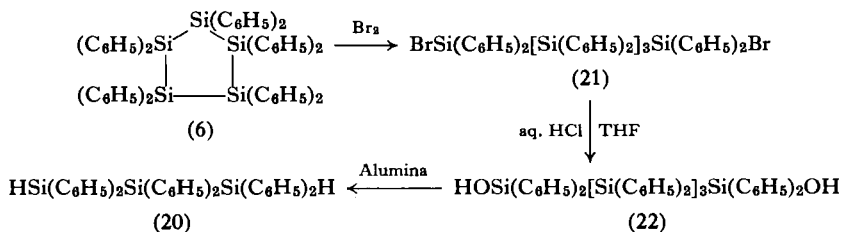
The problem of the molecular weight and structure of Compound "B" was investigated in our Laboratories¹⁸ after the structure of octaphenylcyclotetrasilane had been assigned to Compound "A." We, too, were in error in our first determinations.¹⁸ The molecular weight was initially determined cryoscopically in perylene and by isothermal distillation methods. By the perylene method, a range of 830 to 1270 was obtained for seven determinations with an average value of 1085. This molecular weight indicated that Compound "B" was dodecaphenylcyclohexasilane. The isothermal distillation method also indicated a hexasilane, with values of 1025, 1120, and 1225 being obtained. Three derivatives of Compound "B" were also obtained; they were compounds assigned the structures 1,6-dimethyldodecaphenyl-

hexasilane, 1,6-dibromododecaphenylhexasilane and its hydrolysis product, dodecaphenylhexasilane-1,6-diol.¹⁸ Attempts to prepare the first of these compounds by methods not involving Compound "B" and its derivatives were inconclusive. It might be pointed out that the elemental analysis of these compounds does not provide conclusive evidence for their structure.

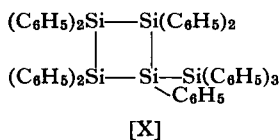
After the above information was published concerning Compound "B,"¹⁸ an investigation into the cleavage of the silicon-silicon bond adjacent to an hydroxy group in polysilanols was being carried out.³⁸ It had been shown previously that when the hydrolysis product of 1,4-dichlorooctaphenyltetrasilane was simply chromatographed on alumina, 1*H*,2*H*-tetraphenyl-disilane could be obtained.³⁹ This reaction appears to be general, because, as an example, 4*H*-octaphenyltetrasilane-1-ol (19), when chromatographed on alumina, gives 1*H*,3*H*-hexaphenyltrisilane (20). Thus when the di-



hydroxy derivative of Compound "B" was submitted to this treatment, the product was 1*H*,3*H*-hexaphenyltrisilane (20), indicating that the compound was actually decaphenylpentasilane-1,5-diol (22) and that Compound "B" is decaphenylcyclopentasilane (6)! This sequence of reactions is also added proof of the structure of decaphenylcyclopentasilane: namely, that it is a



cycle composed of five diphenylsilylene units and not some isomer containing a triphenylsilyl group such as [X]. The dimethyl derivative of Compound "B"¹⁸ was also characterized by its nuclear magnetic resonance spectrum as 1,5-dimethyldecaphenylpentasilane, through determination of the ratio



of phenyl to methyl hydrogens. Finally, molecular weight data have been obtained, with a vapor pressure osmometer,⁴⁰ which agree excellently with the structure assigned to Compound "B."⁴¹ Using benzil as a standard, the molecular weight was determined in benzene at several concentrations and extrapolated to zero concentration. Table II and the accompanying figure (Fig. 1) indicate an experimental molecular weight of 912; that required for decaphenylcyclopentasilane is 911. The molecular weight of

TABLE II
MOLECULAR WEIGHT OF DECAPHENYLCYCLOPENTASILANE IN
BENZENE AT 37.0° C (VAPOR PRESSURE OSMOMETER)

Concentration		Molecular weight
(gm/liter)	(Molar, obs.)	
9.056	0.0100	906
26.58	0.0296	895
54.04	0.0610	886
80.57	0.0915	880

decaphenylcyclopentasilane has also been determined for usebullioscopically in toluene⁴² using octaphenylcyclotetrasilane as a standard,⁴³ and by an X-ray diffraction study and density determination of crystalline decaphenylcyclopentasilane.⁴⁴ The former method gave a value of 921 (average of four values) for the molecular weight of decaphenylcyclopentasilane.⁴³ The X-ray analysis was performed on crystals grown from a mixture of benzene and alcohol, from which the cyclopentasilane crystallizes with one molecule of benzene for each $\text{Si}_5(\text{C}_6\text{H}_5)_{10}$ unit. The value for the molecular weight obtained by this method was 983, which is in good agreement with a value of 989 calculated for decaphenylcyclopentasilane plus one molecule of benzene.⁴⁴

Compound "C," the third crystalline compound isolated by Kipping,¹⁴ has so far resisted structure determination. It was usually isolated in a mixture with octaphenylcyclotetrasilane, from which Compound "C" was separated by fractional crystallization or by conversion of the octaphenylcyclotetrasilane to its more soluble 1,4-diiodide or 1,4-dichloride. Kipping found that Compound "C" did not react with the reagents which attacked octaphenylcyclotetrasilane. Compound "C" was described as a crystalline

material which, when heated in a test tube, did not melt at high temperatures, charred slightly, and gave vapors which took fire with distinct explosion.¹⁴

A material, apparently identical with Kipping's Compound "C," has been isolated in low yield (*ca.* 10%) from the reaction of lithium with dichlorodiphenylsilane.⁴⁵ Small quantities of "C," in agreement with Kipping's observation, can be recrystallized from benzene in which it is only slightly soluble. A better recrystallization solvent has been found in tetralin, in which "C" is more soluble. On allowing such solutions to cool,

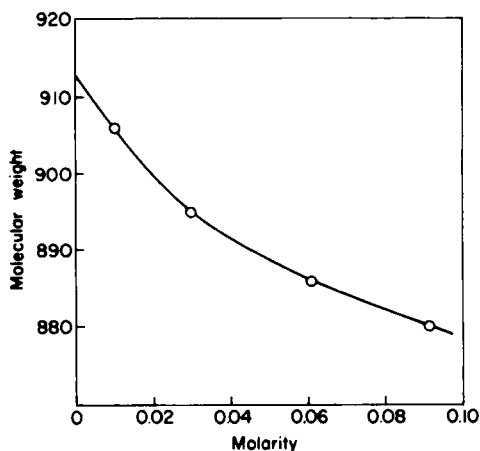
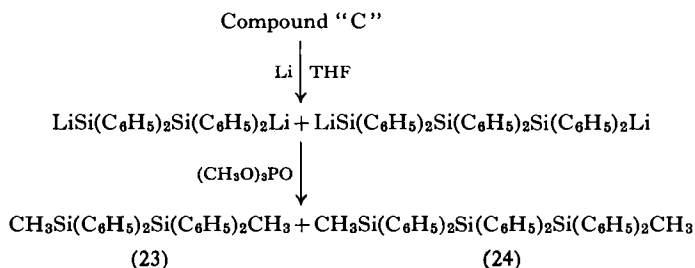


FIG. 1. Molecular weight of decaphenylcyclopentasilane determined at several concentrations and extrapolated to infinite dilution.

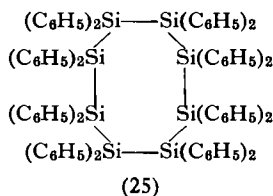
there is deposited microcrystalline Compound "C." Samples treated in this manner were found to melt with marked decomposition at 502–504° C, if they were put into a melting point block at 480° C. Maintaining Compound "C" at temperatures below its melting point for extended periods causes considerable softening and shrinking of the sample.⁴¹

Chemically, Compound "C" is quite inert. In addition to Kipping's observations, it was also found to be unreactive with bromine in refluxing benzene, mercuric chloride in benzene or tetrahydrofuran, and methyl-lithium in tetrahydrofuran-ether mixtures, all of which react readily with octaphenylcyclotetrasilane.⁴¹ Compound "C" has been found to react with lithium in tetrahydrofuran to give a mixture of silyllithium compounds, of which the 1,2- and 1,3-derivatives have been identified by means of their

dimethyl derivatives (23, 24).⁴¹ However, these products cannot be considered to be proof of the structure of Compound "C," since they are probably formed by secondary cleavages. Compound "C" also reacts with an excess of phosphorus pentachloride, and with chlorine in refluxing *sym*-tetrachloroethane or *o*-dichlorobenzene, respectively.⁴¹ However, the products isolated and identified appear to be secondary cleavage products.



Although the structure of Compound "C" has not yet been established, a postulation can be made. Kipping suggested that "C," due to its unreactivity, resembled Compound "B" (decaphenylcyclopentasilane), but was probably more complex. He proposed as possible structures dodecaphenylcyclohexasilane (11) or hexadecaphenylcyclooctasilane (25).¹⁴ The former is a very likely structure, as it is the next in the homologous series of phenylated cyclosilanes and is not an unexpected product in the reaction of dichlorodiphenylsilane with metals. A molecular model of dodecaphenylcyclohexasilane reveals a very compact and tight structure, with the silicon ring



well protected by surrounding phenyl groups. This might explain the low reactivity of Compound "C," below that of an ordinary phenylated disilane linkage as in hexaphenyldisilane. Reagents of small atomic size such as lithium or chlorine might well be able to react with such a structure; however, once the ring is open, the silicon-silicon bonds in the resulting material would be more prone to react with the excess reagent, leading to secondary cleavage products.

One other piece of information has been gathered on the structures of the three perphenylated cyclosilanes. Their infrared spectra (in KBr) in the 5000–700 cm^{-1} range are for all practical purposes identical. The absorption at 1092 cm^{-1} does show a slight shift to longer wavelengths with increasing ring size. However, the spectra are quite different from each other in the 700–200 cm^{-1} region. The infrared spectra of these cyclosilanes, and also 1,5-di-*n*-butyldecaphenylpentasilane, were determined as Nujol mulls using cesium iodide optics (Beckman IR7). All four compounds possess an absorption band at about 476 cm^{-1} which is split into a doublet. Absorption in this region has been attributed to a silicon–phenyl grouping.⁴⁶ The three cyclosilanes also have an absorption centered at 333 cm^{-1} . In octaphenylcyclotetrasilane it appears as a sharp singlet; in decaphenylcyclopentasilane it appears as a reasonably symmetrical multiplet; and in Compound "C" it is a triplet. In 1,5-di-*n*-butyldecaphenylpentasilane absorption at this point is lacking; however, a new strong absorption band appears at 294 cm^{-1} . Absorption in this region has been attributed, in the case of hexaphenyl-disilane, to axial deformation of the two silicon atoms.⁴⁶ Whether the observed data correspond to the same type of absorption is not certain; but, in any case, the spectra seem to indicate similarities between the three cyclosilanes as well as some definite differences.

The structures and properties of the phenylated cyclic polysilanes have been treated in detail because these compounds have been most studied. By analogy to octaphenylcyclotetrasilane and decaphenylcyclopentasilane, the structures for the corresponding *p*-tolyl derivatives reported by Kipping¹⁵ may also be assigned. Therefore, the less soluble, more reactive compound melting at 290–293° C (dec.) is probably octa-*p*-tolylcyclotetrasilane (7), while the more soluble, less reactive, material is probably deca-*p*-tolylcyclopentasilane (8).

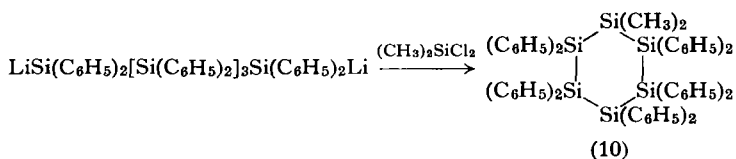
One other organic substituted cyclosilane has been reported in the literature. Burkhard prepared dodecamethylcyclohexasilane (9) by the reaction of dichlorodimethylsilane with sodium in hydrocarbon solvents.¹⁶ Under these conditions, the cyclosilane was formed in low yield along with polymeric materials, one of which was characterized as a dimethylsilylene polymer with an average degree of polymerization of 55 units.^{16, 46a}

Dodecamethylcyclohexasilane was characterized by analysis and molecular weight.⁴⁷ The cyclosilane has also been prepared from dichlorodimethylsilane with sodium⁴⁸ or lithium⁴¹ in tetrahydrofuran. In the latter case, the yield of dodecamethylcyclohexasilane was 33%. Recently, a modi-

fication of this reaction, which will be described subsequently, has increased the yield to 70%.⁴⁹

Dodecamethylcyclohexasilane is a readily sublimable material (*ca.* 100° C) which melts at 250–252° C in a sealed tube. It appears that several crystal changes occur when a sample is heated slowly from room temperature to 200° C. Molecular weight determination with a vapor pressure osmometer gave a value of 349 (calculated 348.9).⁴⁹ The chemistry of dodecamethylcyclohexasilane is at present in only a very preliminary stage. This compound has been shown to react with methyl lithium and with halogenating agents as mild as *sym*-tetrachloroethane to give mixtures of products, which as yet have not been fully elucidated.^{49a}

Another organic substituted cyclosilane has been prepared by the reaction of 1,5-dilithiodecaphenylpentasilane with dichlorodimethylsilane.⁴¹ The resulting product, 1,1-dimethyldecaphenylcyclohexasilane (10), which might be a possible analog of Compound "C," is characterized by its high



melting point (472–476° C) and its relatively low solubility in benzene (less than that of decaphenylcyclopentasilane). When recrystallized from benzene, the crystals retain the solvent firmly, which is also a characteristic, in varying degree, of the other phenylated cyclosilanes.

B. Reactivity of the Si–Si Bond

The chemistry, so far investigated, of the organic substituted cyclosilanes is that involved in the cleavage of the silicon–silicon bond. In these studies, the initial reaction any reagent undergoes with a cyclosilane is ring opening to give the corresponding α,ω -disubstituted polysilane. The resulting polysilanes, of course, still contain silicon–silicon bonds, and the products isolated often depend upon the relative reactivity of the derivatives in further cleavages. The initial ring opening reactions, therefore, concern the chemistry of the silicon–silicon bond with variations due to: (1) substituents attached to silicon; (2) ring size; and (3) steric factors.

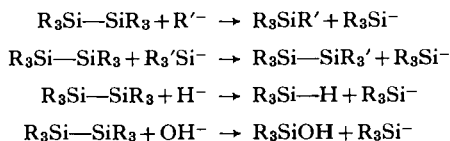
To present a brief survey of the chemistry of the organic substituted silicon–silicon bond, as it bears on the reactions of cyclosilanes which have

been investigated, some general reactions of the organodisilane linkage will be considered. Some of the reactions which disilane systems undergo may be grouped in several classes: cleavage by alkali metals, cleavage by bases, including organometallic and organosilylmetallic reagents; and cleavage by halogens.

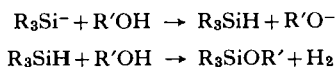
Organic substituted disilanes containing aryl groups are cleaved by alkali metals in ethereal solvents.^{33, 50, 51} Sodium-potassium alloy, rubidium, and cesium will cleave the silicon-silicon bond in arylated disilanes in diethyl ether to give the corresponding silylmetal compounds.⁵²⁻⁵⁶ In ethylene glycol dimethyl ether, sodium and lithium are effective cleaving agents.⁵⁷ However, the method of choice for preparing silyllithium compounds is the cleavage of a disilane with lithium in tetrahydrofuran.⁵⁸⁻⁶⁰ Such solutions are easily handled and are reasonably stable.⁶¹ This system has been used quite extensively to investigate the perphenylated cyclosilanes.

Although silicon-silicon bond cleavage of halogenated polysilanes by organometallic reagents has long been known,⁶² the cleavage of hexaaryl-disilanes by organolithium compounds, even though it has been observed to take place,⁶³ cannot be considered a facile reaction. The reactions of hexaalkyldisilanes with organometallic reagents has not as yet been adequately investigated. Arylated disilanes are also cleaved by silyllithium compounds⁶⁴ and by lithium aluminum hydride in tetrahydrofuran.^{49a}

Scission of the silicon-silicon bond of disilanes is also achieved through the agency of aqueous or methanolic alkali,^{2, 65} aqueous piperidine,^{25, 26} and alkali in hexanol.¹⁶ All of these reactions can be considered as an attack of a basic or nucleophilic species and are represented generally as follows:



The last reaction is carried out in hydroxylic media, which effects immediate hydrolysis of the intermediate silyl anion to an Si-H compound which is in turn hydrolyzed to a silanol with evolution of hydrogen.⁶⁶ That a silicon hydride can be an intermediate in such reactions is shown in the cleavage of polysilanol on alumina,^{38, 39} which can be considered to a mildly basic reagent.



Not considering resonance effects,¹ it would appear that inductively withdrawing substituents such as chlorine atoms or hydroxyl groups^{38, 39, 67} on a silicon atom aid in nucleophilic attack at this site.

Halogens cleave the Si—Si bond of disilanes with varying ease, depending upon the substituents on silicon and upon the halogen. Thus, the relative reactivity of halogens with a given silicon-silicon bond appears to be $\text{Cl} > \text{Br} > \text{I}$.⁶⁸ This order of reactivity is probably due to the relative coordinating ability of the halogens with silicon in a pentacovalent state, possibly due to steric limitations.¹

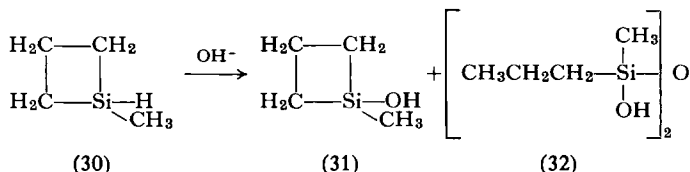
Hexaaryldisilanes are fairly resistant to cleavage by halogens,^{55, 69–71} although hexaphenyldisilane reacts slowly with bromine in carbon tetrachloride.⁷¹ Hexaalkyldisilanes, on the other hand, are rather easily cleaved by halogens.^{54, 68, 72} Also, substitution of alkyl groups by halogen on the disilane linkage reduces the rate of cleavage to a marked degree.⁷² For example, the cleavage of 1,2-dichlorotetramethyldisilane by bromine is about 100 times slower than that of hexamethyldisilane under the same conditions.⁶⁸

In contrast to the analogous hexarylethanes, hexaaryldisilanes show no tendency to dissociate into radicals¹ and, therefore, do not react with oxygen, with oxidizing agents such as selenium dioxide and lead tetraacetate, or with iodine in boiling xylene.^{55, 70, 71, 73, 74}

C. Ring Strain

The reactivity of octaphenylcyclotetrasilane has been attributed to "ring strain and the accompanying homolytic cleavage to a biradical."¹⁷ This explanation may be an oversimplified statement of the mechanism of reaction involved in the ring opening, and it is not necessarily true that a biradical species is involved. First of all, to take a specific example, hexaphenyldisilane shows no tendency to dissociate into free radicals, as does hexaphenylethane, even though the silicon-silicon bond is considered to be inherently weak compared with a carbon-carbon bond.^{1, 75} Secondly, granted that ring strain may increase the reactivity of octaphenylcyclotetrasilane due to distortion of the tetrahedral bond angles of silicon, this effect need not be so important as it is in carbon chemistry.⁷⁶ The tetrahedral angle of silicon is believed to be more easily deformed than that of carbon.⁷⁷ And, thirdly, if octaphenylcyclotetrasilane were incipiently disposed to dissociate into a biradical species under reasonably normal conditions due

1-methylsilacyclobutane (30) compared to higher homologs and to normal trialkylsilanes⁸² by structure-reactivity relations resulting from *steric factors*; this explanation can be applied directly to octaphenylcyclotetrasilane, with ring opening being the exclusive reaction.



Therefore, if the silicon atom of octaphenylcyclotetrasilane which is undergoing attack by a reacting species is considered to attain a pentacovalent configuration (Fig. 2), the following three factors assist in the subsequent

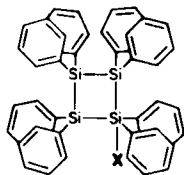


FIG. 2. Pentacovalent intermediate involved in the attack of octaphenylcyclotetrasilane by various reactants.

cleavage of a silicon-silicon bond: (a) ease of formation of pentacovalent silicon resulting from other groups being "pulled back" away from the path of reagent attack; (b) lack of angular strain⁸³ at the pentacovalent silicon atom relative to the tetracovalent state; and (c) lack of appreciable added steric interactions in the complex over that in the substrate, the added strain being less in a four-membered ring than in a larger one.

All of these factors aid in the formation of the pentacovalent silicon, with ring strain in octaphenylcyclotetrasilane promoting formation of the complex rather than directly causing ring opening. For decaphenylcyclopentasilane, increased crowding of phenyl groups tends to prevent approach of reagents, bond angles are not as well disposed for formation of a pentacovalent intermediate, and added steric interactions between phenyl groups in the complex should be appreciable. In hexaphenyldisilane, severe crowding of phenyl groups as a pentacovalent state is approached might serve to explain its relative stability toward iodine and bases.

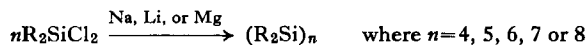
While this discussion assumes the formation of a discrete pentacovalent state, it may be pointed out that any mechanism which provides a closer approach to such an intermediate would permit a lower energy profile and, therefore, indicate a more facile reaction. This might explain, for example, the greater reactivity of bromine with decaphenylcyclopentasilane over that of hexaphenyldisilane.

IV

FORMATION OF THE CYCLOSILANES

A. From Dichloromonosilanes and Metals

In general, all of the organic substituted cyclosilanes have been prepared by the reaction of a dichlorodiorganosilane with lithium, sodium, or magnesium, using various solvents. The perarylated cyclosilanes were first prepared by F. S. Kipping by the action of sodium on dichlorodiphenylsilane



and dichlorodi-*p*-tolylsilane in refluxing toluene or xylene.¹³⁻¹⁵ From the former reaction, octaphenylcyclotetrasilane^{17, 35} and decaphenylcyclopentasilane,¹⁷⁻¹⁹ as well as Compound "C," have been isolated. From the latter reaction, octa-*p*-tolylcyclotetrasilane and deca-*p*-tolylcyclopentasilane are suggested as structures of two of the compounds isolated, by comparison with their phenylated analogs. Octaphenylcyclotetrasilane was also obtained from the reaction of chlorophenoxydiphenylsilane with sodium.²⁴

Together with the solid phenylated cyclosilanes isolated from these reactions, there were also obtained rather large quantities of viscous liquid materials which have not as yet been fully characterized.²³ Partial separation of these oils was achieved by fractionation from acetone. Some less soluble portions appeared to be materials made up of only diphenylsilylene units. Cryoscopic determinations of various fractions indicated multiples of $Si(C_6H_5)_2$ ranging from seven to nine, and chemical evidence seemed to indicate that the materials were cyclic polysilanes.²³

Octaphenylcyclotetrasilane has also been prepared by the action of magnesium on dichlorodiphenylsilane in tetrahydrofuran³⁴; however, the method of choice is the reaction of the dichlorosilane with lithium in tetrahydrofuran.¹⁷ An improved procedure has been developed by which either

octaphenylcyclotetrasilane or decaphenylcyclopentasilane can be prepared in high yield.⁸⁴ The technique involves the maintenance of a small amount of silyllithium species throughout the preparation in tetrahydrofuran. Under these conditions, when an equivalent amount of dichlorodiphenylsilane is added to lithium, the reaction is highly exothermic and octaphenylcyclotetrasilane can be isolated in yields up to 60%.⁸⁴ If a slight excess of lithium is used under the same conditions and the reaction mixture is refluxed for 3 hours subsequent to combining the reactants, octaphenylcyclotetrasilane is converted to decaphenylcyclopentasilane. This latter product has been obtained in nearly quantitative yield.⁸⁴ Also, small amounts of Compound "C" are isolated in these reactions.

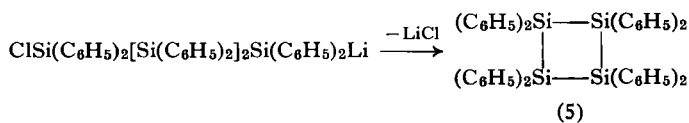
A number of precursory compounds can be visualized in the formation of octaphenylcyclotetrasilane from the reaction of dichlorodiphenylsilane with a metal such as lithium (Table III).

TABLE III

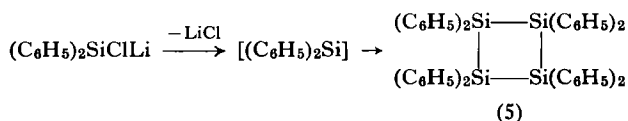
POSSIBLE INTERMEDIATES IN THE FORMATION OF OCTAPHENYLCYCLOTETRASILANE

$(\text{C}_6\text{H}_5)_2\text{SiClLi}$	$\text{ClSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Cl}$
$(\text{C}_6\text{H}_5)_2\text{Si}$	$\text{ClSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Li}$
$(\text{C}_6\text{H}_5)_2\text{SiLi}_2$	$\text{LiSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Li}$
$\text{ClSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Cl}$	$\text{ClSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Cl}$
$\text{ClSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Li}$	$\text{ClSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Li}$
$\text{LiSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Li}$	$\text{LiSi}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Li}$

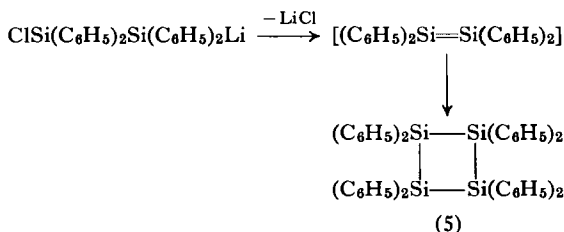
One of the simplest intermediates is chlorodiphenylsilyllithium $[(\text{C}_6\text{H}_5)_2\text{SiClLi}]$. This compound may undergo a variety of reactions, among which are the following: (a) reaction with itself to give 1-chloro-2-lithiotetraphenyldisilane; (b) reaction with dichlorodiphenylsilane to give 1,2-dichlorotetraphenyldisilane; (c) reaction with many of the other suggested possibilities in Table III, providing a chain-lengthening scheme in which the final step leading to octaphenylcyclotetrasilane is most probably ring closure of 1-chloro-4-lithiooctaphenyltetrasilane.



Chlorodiphenylsilyllithium can be depicted in other conversions, such as: (d) reaction with lithium metal to give dilithiodiphenylsilane $[(C_6H_5)_2SiLi_2]$, a species of undoubtedly high reactivity, which could undergo the same type of silicon chain-propagating steps described for chlorodiphenylsilyllithium; (e) elimination of lithium chloride to give diphenylsilylene $[(C_6H_5)_2Si]$, which might in turn "polymerize" to octaphenylcyclotetrasilane. Studies concerned with this latter proposal are in progress in our Laboratories, and an interpretation of some of these reactions does not exclude the possibility that diphenylsilylene may be formed transitorily.

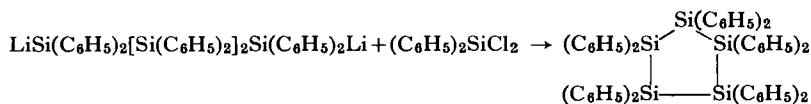


There also exists the remote possibility of the intermediate formation of a Si=Si type which might be expected to dimerize to octaphenylcyclotetrasilane. Other possibilities for the formation of octaphenylcyclotetrasilane involve not only interaction of some combinations of the compounds



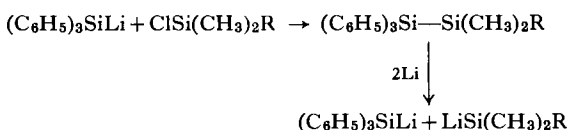
in Table III, but also reactions of some of them with dichlorodiphenylsilane or with lithium metal.

Whatever may be the mode of formation of octaphenylcyclotetrasilane, it appears that this compound can be a precursor of decaphenylcyclopentasilane. Evidence for such a conversion has already been presented in the facile formation of decaphenylcyclopentasilane from octaphenylcyclotetrasilane by the agency of small quantities of lithium metal.⁸⁴ The cyclopentasilane is formed in high yield from dichlorodiphenylsilane and 1,4-dilithio-octaphenyltetrasilane, which is prepared from octaphenylcyclotetrasilane.⁸⁵

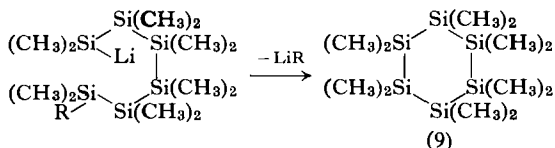


Dodecamethylcyclohexasilane was first prepared¹⁶ by the reaction of sodium with dichlorodimethylsilane in benzene in an unspecified yield along with a considerable amount of hydrocarbon-insoluble dimethylsilylene polymer. This cyclosilane has also been prepared from lithium⁴¹ or sodium⁴⁸ and dichlorodimethylsilane in tetrahydrofuran. A recent modification of this reaction, employing a catalytic amount of triphenylsilyllithium, has increased the yield of the cyclosilane to 70% with essentially no formation of the insoluble polymer.⁴⁹

The proposed mechanism for the catalysis by triphenylsilyllithium is illustrated in the following scheme, where R is Cl, Si(C₆H₅)₃, [Si(CH₃)₂]_nCl, or [Si(CH₃)₂]_nSi(C₆H₅)₃:



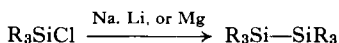
The cyclization reaction can then be represented, when R is Cl or Si(C₆H₅)₃, as follows:



Other permethylated cyclosilanes might be expected to form in this reaction, and there is some preliminary evidence that the corresponding cyclopentasilane and cycloheptasilane are minor products of the reaction; however, these materials have not been fully investigated.⁴⁹

B. By Cyclization of α,ω -Dihalopolysilanes with Metals

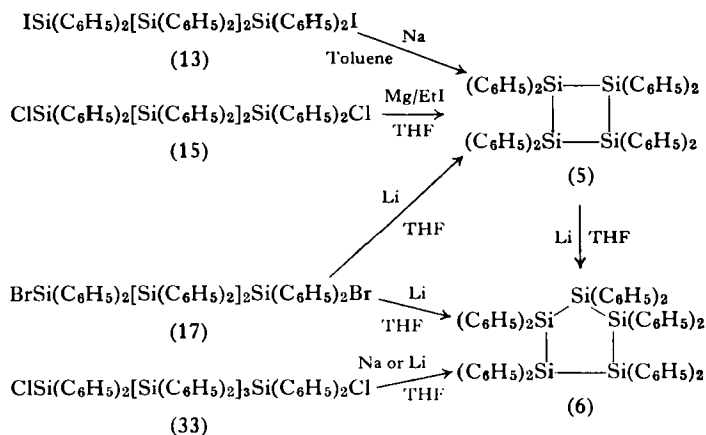
A common method for the formation of silicon-silicon bonds is the reaction of a halosilane with metals such as sodium,¹ lithium,³⁴ or magnesium.^{86, 26} This method has been tried with some success in the case of the phenylated α,ω -dihalopolysilanes to give cyclic products; however, the reaction is not necessarily so straightforward as would be desired.



Kipping carried out the first reaction of this type in the formation of octaphenylcyclotetrasilane (5) from 1,4-diiodooctaphenyltetrasilane (13) and sodium in refluxing toluene.¹³ However, 1,4-dibromooctaphenyltetra-

silane (17) does not react with sodium under similar conditions.⁸⁷ 1,4-Dibromooctaphenyltetrasilane (17) with excess lithium in tetrahydrofuran (THF) gives octaphenylcyclotetrasilane (5) and decaphenylcyclopentasilane (6) in 16% and 53% yields, respectively. When an equivalent amount of lithium is used, the same products are isolated in 30% and 25% yields, respectively.⁸⁷ By the reaction of magnesium with 1,4-dichlorooctaphenyltetrasilane (15) in tetrahydrofuran (THF) in the presence of ethyl iodide, octaphenylcyclotetrasilane can be obtained in 39% yield.⁸⁷

1,5-Dichlorodecaphenylpentasilane (33) is converted into decaphenylcyclopentasilane (6) by sodium or lithium in tetrahydrofuran.⁸⁷ Magnesium in the presence of ethyl iodide has proved⁸⁸ to be a better cyclizing reagent, giving yields of the cyclosilane up to 83%.

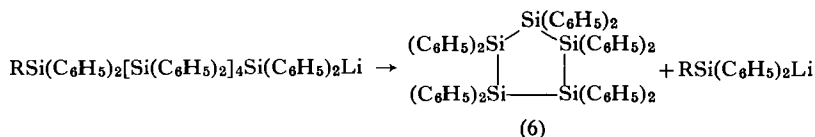


Attempts to prepare hexaphenylcyclotrisilane by reaction of 1,3-dichlorohexaphenyltrisilane with sodium in refluxing xylene or with magnesium in tetrahydrofuran resulted only in a variety of products, including octaphenylcyclotetrasilane, decaphenylcyclopentasilane, and Compound "C."⁴¹ No product so far isolated could be ascribed the structure of the cyclotrisilane, a highly strained ring system.

C. Other Cyclization and Conversion Reactions

The special case of conversion of octaphenylcyclotetrasilane to decaphenylcyclopentasilane has been observed in reactions of the former compound with alkyl-⁸⁹ and aryllithium⁹⁰ compounds, triphenylsilyllithium,⁹⁰ and lithium aluminum hydride,^{49a} as well as with lithium metal.⁸⁵

All of these reactions depend upon the fact that octaphenylcyclotetrasilane reacts readily with these reagents while decaphenylcyclopentasilane is relatively stable to them. The same type of an intermediate, namely, a polysilyllithium compound which can undergo intramolecular cyclization to give the cyclopentasilane (6), is probably produced in each case.



V

GENERAL REACTIONS OF THE CYCLOSILANES

Organic substituted cyclosilanes generally undergo reactions which are common to organosilanes, though considerations such as ring size and steric limitations may be important.

A. Reactions with Lithium Metal

The perphenylated cyclosilanes are readily cleaved by lithium metal in tetrahydrofuran to give silyllithium compounds.^{17, 18, 41} These compounds have been used in the structure proof of the cyclosilanes, and also as intermediates in preparing a variety of polyphenylated silanes, with various chain lengths and functional groups.^{17, 18, 41, 90a, 91} Due consideration must be taken of secondary cleavage reactions, which can lead to a variety of silyllithium compounds. Dodecamethylcyclohexasilane (9) does not appear to react with lithium alone in tetrahydrofuran; however, the presence of catalytic amounts of triphenylsilyllithium along with lithium metal does produce extensive reaction, leading to products which have not as yet been thoroughly characterized.^{49a}

B. Halogenation Reactions

Halogenation of the organic substituted cyclosilanes has also been used extensively in characterization of these compounds and to provide silicon-functional compounds for further studies. Octaphenylcyclotetrasilane has

been found to react with iodine,^{13, 17} bromine,⁹² and chlorine.⁹⁵ The extreme reactivity of octaphenylcyclotetrasilane is exemplified in its relatively facile halogenation by various reagents which can be considered as mild halogenating agents. Thus, a wide variety of halogenated hydrocarbons,^{13, 28, 84} inorganic halides,^{28, 93, 95} and the hydrogen halides⁹⁴ effect the cleavage of octaphenylcyclotetrasilane to give halogenated derivatives. Decaphenylcyclopentasilane is much more stable to halogenating reagents; however, it is readily cleaved by bromine^{13, 18, 41} and rapidly reacts with chlorine.⁹⁵ It also reacts with phosphorus pentachloride⁹⁵ in either carbon tetrachloride or *sym*-tetrachloroethane. Chlorination occurs with *sym*-tetrachloroethane alone when extended reaction times are used.⁹⁵

Dodecamethylcyclohexasilane reacts readily with halogenating agents, such as mercuric chloride, phosphorus pentachloride, and *sym*-tetrachloroethane to give a variety of chlorosilane products.^{49a}

C. Reactions with Bases

The cyclosilanes are generally cleaved by various reagents which can be considered to be bases or nucleophilic reagents. Thus, organolithium and organosilyllithium compounds,⁸⁸ methylenetriphenylphosphorane,⁹⁶ lithium aluminum hydride,^{49a} and hydroxylic bases¹³ bring about the cleavage of the silicon-silicon bond. The relative ease of reaction depends upon the substituents on silicon and ring size. These reactions will be taken up more fully in the following sections.

D. Miscellaneous Reactions

Numerous other reactions of the known cyclosilanes have been investigated, with many being specific for octaphenylcyclotetrasilane. Some of these will be considered. A variety of oxygen-containing oxidizing agents easily react with octaphenylcyclotetrasilane, bringing about silicon-silicon bond scission, and leading to the formation of siloxanes.^{13, 28} Other cyclosilanes are stable to these reagents under similar conditions. Octaphenylcyclotetrasilane also undergoes reduction reactions with hydrogen under relatively high pressure using a "copper chromite" catalyst,⁹⁷ and with lithium aluminum hydride.^{49a}

When decaphenylcyclopentasilane is heated strongly in the absence of air, the compound decomposes to give tetraphenylsilane, triphenylsilane, and

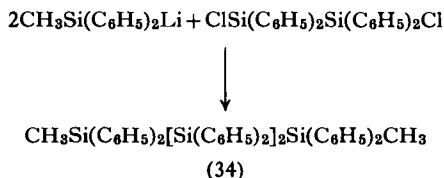
a resinous material.⁹⁸ If the decomposition is attempted under low pressure, the compound only sublimes. Tetraphenylsilane and triphenylsilane are also products of the thermal decomposition of octaphenylcyclotetrasilane; however, apparently no decaphenylcyclopentasilane is formed.⁹⁸

VI

REACTIONS OF OCTAPHENYLCYCLOTETRASILANE

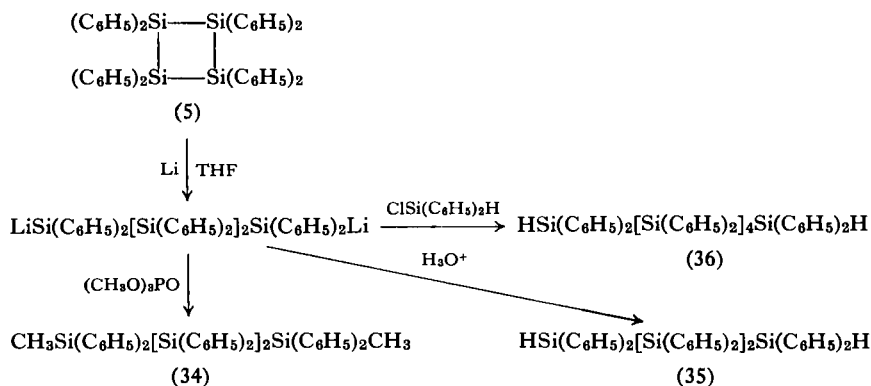
A. With Lithium Metal

Octaphenylcyclotetrasilane reacts readily with lithium metal in tetrahydrofuran to give a mixture of silyllithium compounds.¹⁷ No starting material is usually recovered; however, treatment of such solutions with trimethyl phosphate⁹⁹ provided only 27% of 1,4-dimethyloctaphenyltetrasilane (34),¹⁷ indicating a fairly low yield of 1,4-dilithiooctaphenyltetrasilane. The 1,4-dimethyl derivative (34) was also obtained from the reaction of methyldiphenylsilyllithium with 1,2-dichlorotetraphenyldisilane;¹⁷ this reaction provided a structure proof for the dimethyl compound.

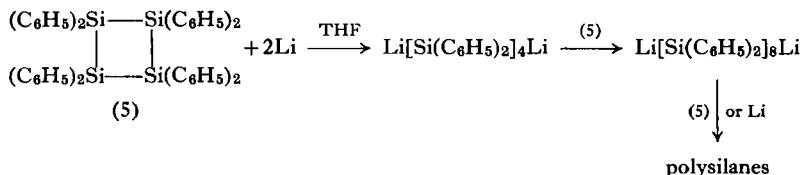


Decaphenylcyclopentasilane is the major product obtained when dichlorodiphenylsilane is added to the lithium cleavage products of octaphenylcyclotetrasilane.⁸⁵ Although this result is not unexpected, its significance regarding the relationship of octaphenylcyclotetrasilane and decaphenylcyclopentasilane is lessened by the fact that the cleavage of the cyclotetrasilane results in a variety of silyllithium compounds. Also, 1*H*,4*H*-octaphenyltetrasilane (35) and 1*H*,6*H*-dodecaphenylhexasilane (36) have been obtained in yields of about 25% by treating the silyllithium compounds produced in the lithium cleavage with dilute hydrochloric acid³⁵ and with chlorodiphenylsilane,¹⁰⁰ respectively. That other disilyllithium compounds are present in these solutions is indicated by the isolation, in low yields, of 1*H*,2*H*-tetraphenyldisilane from the reaction mixture hydrolyzed

with acid; and 1*H*,5*H*-decaphenylpentasilane⁹¹ from the reaction with chlorodiphenylsilane. The residues from such reactions consisted of intractable mixtures of polysilanes.



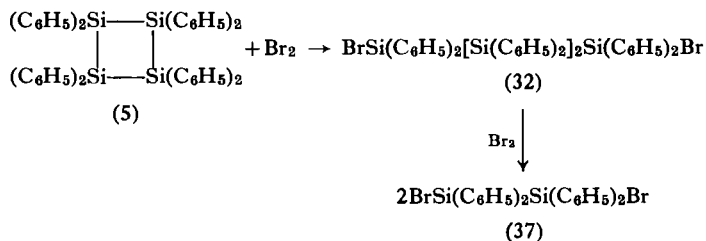
The variety of products isolated from such reactions can be explained by the ready reaction of octaphenylcyclotetrasilane with silyllithium compounds.⁹⁰ Thus, 1,4-dilithiooctaphenyltetrasilane formed by the initial lithium cleavage of octaphenylcyclotetrasilane is able to cleave more octaphenylcyclotetrasilane. Also, cleavage of the α,ω -dilithio compounds by lithium can increase the variety of disilanyl lithium compounds, which can in turn cleave octaphenylcyclotetrasilane, leading to a wide distribution of



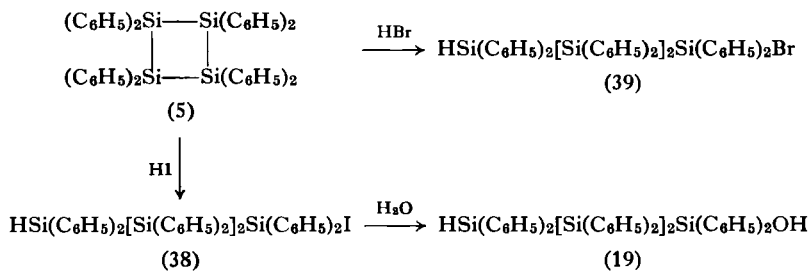
polysilanes. 1,4-Dilithiooctaphenyltetrasilane can also be prepared directly from dichlorodiphenylsilane and an excess of lithium in tetrahydrofuran, probably through octaphenylcyclotetrasilane as an intermediate.³⁴ Derivatives of the disilanyl lithium compound prepared in this manner were obtained by reaction with *n*-butyl chloride, with dimethyl sulfate, and with chlorotrimethylsilane to give 1,4-di-*n*-butyloctaphenyltetrasilane, 1,4-dimethyloctaphenyltetrasilane, and 1,1,1,6,6,6-hexamethyloctaphenylhexasilane, respectively. None of these compounds was isolated in yields greater than 33%.³⁴

B. With Halogens and Hydrogen Halides

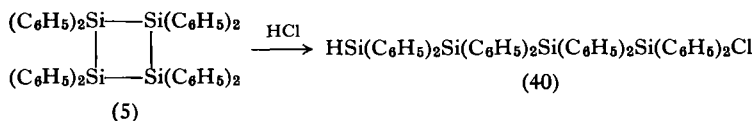
The facile reaction of octaphenylcyclotetrasilane with halogens was first discovered by Kipping, who observed the rather surprising reaction with iodine.^{13, 17} Octaphenylcyclotetrasilane has also been found, not unexpectedly, to be more reactive with bromine in benzene. If equimolar amounts of reactants are used, the product is 1,4-dibromooctaphenyltetrasilane (17); however, if two moles of bromine to one of octaphenylcyclotetrasilane are used, 1,2-dibromotetraphenyldisilane (37) can be isolated in yields up to 85%.⁹² Chlorine quantitatively cleaves the cyclotetrasilane in carbon tetrachloride within 2½ minutes to give 1,4-dichlorooctaphenyltetrasilane.⁹⁵



Octaphenylcyclotetrasilane is also cleaved by hydrogen halides,⁹⁴ although not with the facility observed for the halogens. Both hydrogen iodide and hydrogen bromide react with the cyclotetrasilane in refluxing benzene to give 1*H*-4-iodooctaphenyltetrasilane (38) and 1*H*-4-bromooctaphenyltetrasilane (39). The iodosilane was not isolated, but was hydrolyzed and characterized as 4*H*-octaphenyltetrasilan-1-ol (19).⁹⁴ The bromosilane (39) is obtained in 85% yield.⁹⁴ Hydrogen chloride reacts slowly with octaphenylcyclotetrasilane in refluxing benzene with only 2% of 1*H*-4-chlorooctaphenyltetrasilane (40) being isolated under conditions similar to those used in the hydrogen bromide reaction. However, the utilization of

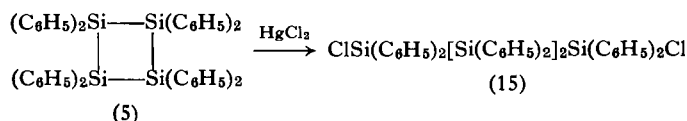


refluxing *o*-dichlorobenzene as solvent provides yields of the chlorosilane (40) approaching 90%.⁹⁴

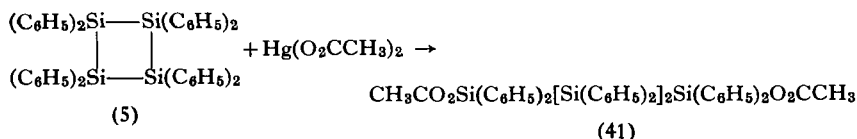


C. With Inorganic Halides and Metal Salts

Some inorganic halides and metal salts in which the central atom can have different oxidation states have the ability to break the silicon-silicon bond in octaphenylcyclotetrasilane. Thus, mercuric chloride reacts with the cyclotetrasilane in benzene to give 92% of 1,4-dichlorooctaphenyltetrasilane (15) and 94% of mercurous chloride.⁹³ Mercuric bromide, mercuric iodide,



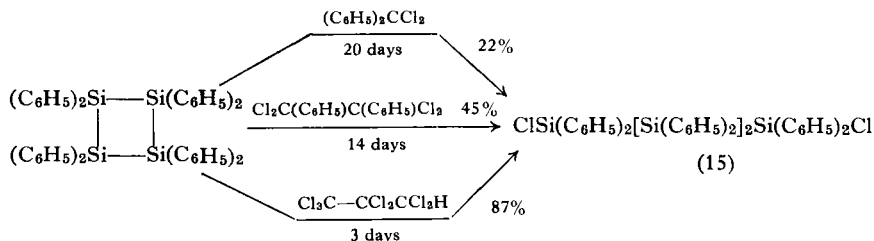
and stannic chloride have been observed to react in a similar manner.⁹³ In refluxing benzene or xylene, phosphorus pentachloride has also been found to react with octaphenylcyclotetrasilane with the production of 1,4-dichlorooctaphenyltetrasilane (15) and phosphorus trichloride.⁹⁵ Phosphorus trichloride does not react with octaphenylcyclotetrasilane under the same conditions.⁹⁵ Mercuric acetate is reduced to give 1,4-diacetoxyoctaphenyltetrasilane (41) and mercury metal.¹⁰¹



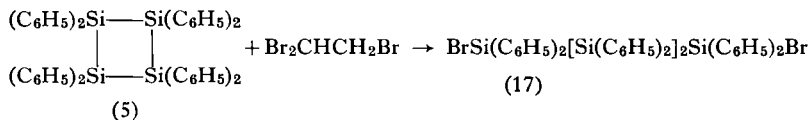
D. With Organic Halides

The observation of Kipping that octaphenylcyclotetrasilane reacts readily with *sym*-tetrachloroethane¹³ and 1,2-dibromoethane,²⁸ has been extended to a large variety of halogenated hydrocarbons.⁸⁴ A wide spectrum of halogenated methanes, ethanes, and propanes has been used. The ease of reaction appears to be dependent on several factors, including the number

of carbon and halogen atoms in the alkyl halide, the nature of the halogen, and the reaction temperature. To illustrate, dichlorodiphenylmethane gave 22% of 1,4-dichlorooctaphenyltetrasilane (15) after 20 days at 80°C; 1,1,2,2-tetrachlorodiphenylethane gave 45% of the same product after 13 days at the same temperature; and heptachloropropane gave 87% of the dichloro derivative (15) after 4 days under the same conditions.⁸⁴ The course



of these chlorination reactions is indicated by the isolation of tetraphenyl-ethylene, in the case of dichlorodiphenylmethane, and the corresponding dehalogenated olefins in the case of the vicinal dichlorohydrocarbons. Temperature has a marked effect on the rate of reaction. Thus, after 10 days



at 80°C, 1,1,2-tribromoethane cleaves octaphenylcyclotetrasilane to the extent of 67% to give 1,4-dibromooctaphenyltetrasilane (17); however, at 188°C the reaction is complete within 6 minutes. Chlorinated ethylenic compounds, where the chlorine is attached to an unsaturated carbon, are incapable of significant reaction with octaphenylcyclotetrasilane even under extended reaction conditions.⁸⁴

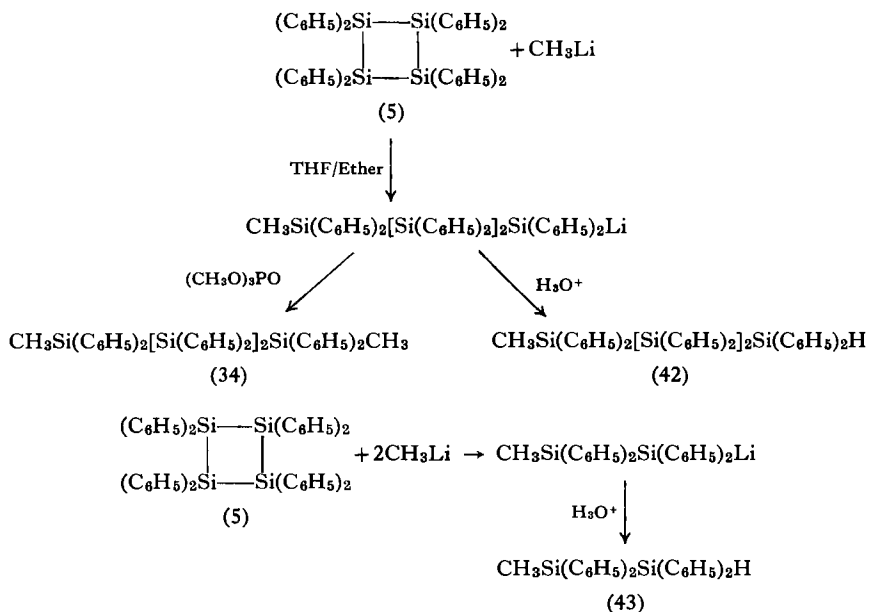
E. With Organometallic and Organosilylmetallic Reagents

Octaphenylcyclotetrasilane is cleaved by phenyllithium in a tetrahydrofuran-ether mixed solvent system.⁹⁰ When equimolar quantities of the reactants are stirred for 5 hours, 55% of the octaphenylcyclotetrasilane is recovered and decaphenylcyclopentasilane is obtained in 18% yield.

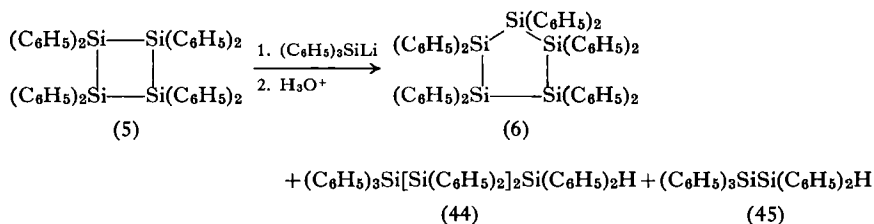
However, when five equivalents of phenyllithium are used for extended reaction times, the major product isolated after hydrolysis is pentaphenyl-

disilane, indicating the formation of pentaphenyldisilanyllithium.⁹⁰ Of course, in these reactions, as in the lithium cleavage of octaphenylcyclotetrasilane, a great variety of polysilanyllithium compounds is possible.

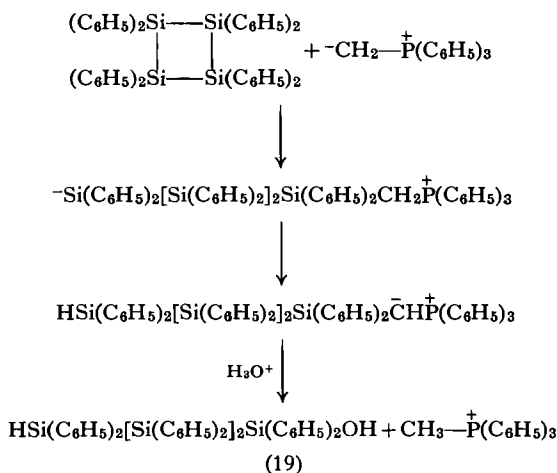
Methylolithium also cleaves octaphenylcyclotetrasilane in a tetrahydrofuran-ether solvent.¹⁰² Two equivalents of methylolithium bring about cleavage within 30 minutes to give 1-lithio-4-methyloctaphenyltetrasilane in yields up to 66%, as indicated by derivative formation using trimethyl phosphate to obtain 1,4-dimethyloctaphenyltetrasilane (34). Acid hydrolysis of the reaction mixture leads to 1*H*-4-methyloctaphenyltetrasilane (42) in comparable yield. The use of a longer reaction time and a large excess of methylolithium leads to 1*H*-2-methyltetraphenyldisilane (43) as the major product (65%), after acid hydrolysis.¹⁰²



Octaphenylcyclotetrasilane reacts with triphenylsilyllithium to give, subsequent to acid hydrolysis, decaphenylcyclopentasilane and a product tentatively identified as 1*H*-nonaphenyltetrasilane (44).⁹⁰ Excess triphenylsilyllithium and extended reaction time gave hexaphenyldisilane and pentaphenyldisilane (45) in moderate yields.⁹⁰ The products isolated from these reactions establish that secondary cleavages have taken place under the conditions used.



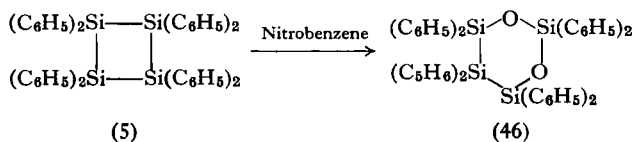
Octaphenylcyclotetrasilane also reacts with methylenetriphenylphosphorane with ring opening to give as a product, after acid hydrolysis, 4*H*-octaphenyltetrasilan-1-ol (19).⁹⁶ This compound is depicted as arising through the following reaction scheme.



F. With Oxidizing Agents

Although many reactions involving ring opening of the cyclosilanes can be considered to involve oxidation, a special case of oxidation of octaphenylcyclotetrasilane has been observed with oxygen and oxygen-containing compounds. Kipping found that octaphenylcyclotetrasilane is rapidly attacked by refluxing nitrobenzene to give a dioxide¹³ as the major product, which has since been suggested to be octaphenyl-1,3-dioxacyclohexasilane (46).²⁹ The ease of oxidation is demonstrated by the fact that the cyclosilane is oxidized by air at room temperature to give octaphenyloxacyclopentasilane and a glue-like polymer, evidently siloxanes.²⁸ Octaphenylcyclotetrasilane is oxidized by air in toluene at 100°C and by ozonized oxygen in carbon

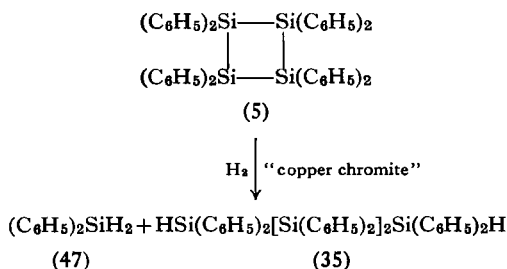
tetrachloride or carbon disulfide. From these reactions octaphenyloxacyclopentasilane and octaphenyl-1,4-dioxacyclohexasilane were isolated.²⁸



Benzaldehyde causes rapid oxidation of octaphenylcyclotetrasilane, while benzyl alcohol, acetophenone, paraldehyde, and amyl nitrite react slowly. Again, the products from these reactions are the cyclic monoxide and dioxide along with varying amounts of viscous polymers.²⁸ Octaphenylcyclotetrasilane appears to be stable to aqueous oxidizing agents such as potassium permanganate and potassium dichromate; however, this may be due to the insolubility of the compound in the aqueous media employed.

G. With Hydrogen

Hydrogenolysis of octaphenylcyclotetrasilane occurs under conditions of relatively high temperature and pressure in the presence of chromium-containing catalysts.^{49a} Thus, with a "copper chromite" catalyst at 150° C under about 800 psi pressure, 42–48% of diphenylsilane (47) and 5–12% of 1*H*,4*H*-octaphenyltetrasilane (35) were isolated. In the absence of a catalyst at 250° C and 1450 psi pressure, octaphenylcyclotetrasilane undergoes very little reaction with hydrogen, with 84% of the starting material being recovered. Raney nickel, palladium on carbon, and carbon are ineffective as catalysts.^{49a}



For comparison, hexaphenyldisilane in the presence of "copper chromite" catalyst undergoes hydrogenolysis at 150° C and 850 psi pressure to give

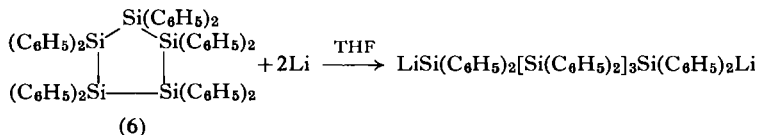
17% of triphenylsilane and 59% of recovered starting material. Hexaethyldisilane, under the same conditions, is unaffected.⁹⁴ Decaphenylcyclopentasilane is more resistant to hydrogenolysis under these conditions than is hexaphenyldisilane.^{49a}

VII

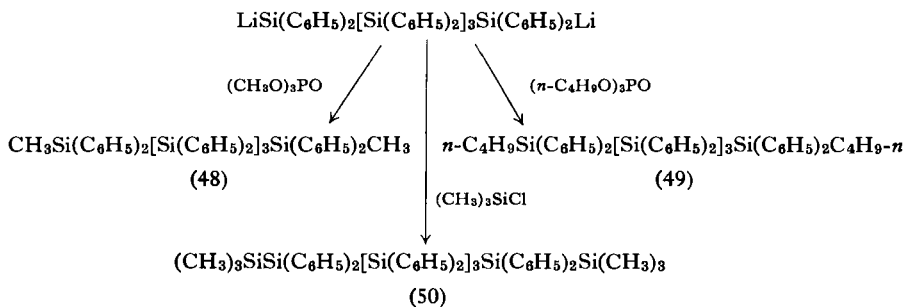
REACTIONS OF DECAPHENYLCYCLOPENTASILANE

A. With Lithium Metal

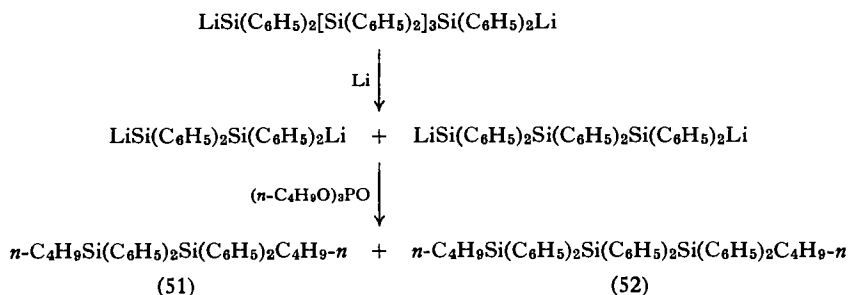
Decaphenylcyclopentasilane, like octaphenylcyclotetrasilane, is easily cleaved by lithium in tetrahydrofuran (THF).^{18, 41} However, in this case, the reaction is more straightforward than with octaphenylcyclotetrasilane. 1,5-Dilithiodecaphenylpentasilane is formed in good yields, as indicated by a double titration method involving either allyl bromide¹⁰³ or *n*-butyl bromide¹⁷ and by derivative formation with a variety of reagents. Yields of the lithium cleavage product determined by titration are close to the theoretical, based on the following reaction.



The use of trimethyl phosphate,⁹⁹ tri-*n*-butyl phosphate,⁹⁹ and chlorotrimethylsilane (reagents which generally react with silyllithium compounds with a minimum of side reactions) gave 1,5-dimethyldecaphenylpentasilane (48),^{18, 41} 1,5-di-*n*-butyldecaphenylpentasilane (49),⁴¹ and 1,1,1,7,7,7-hexamethyldecaphenylheptasilane (50),⁴⁰ respectively, in 80–85% yields.



The lithium cleavage of decaphenylcyclopentasilane is complete in about 2 hours. Shorter reaction times lead to recovered starting material, while longer times allow secondary cleavage reactions to occur. For example, using a 4.5 hour cleavage time, a 63% yield of 1,5-di-*n*-butyldecaphenylpentasilane (49) and about 5% each of 1,2-di-*n*-butyltetraphenylidisilane (51) and 1,3-di-*n*-butylhexaphenyltrisilane (52)⁴¹ were obtained, subsequent to reaction with tri-*n*-butyl phosphate. Evidently, the latter two products arise from lithium cleavage of 1,5-dilithiodecaphenylpentasilane, a



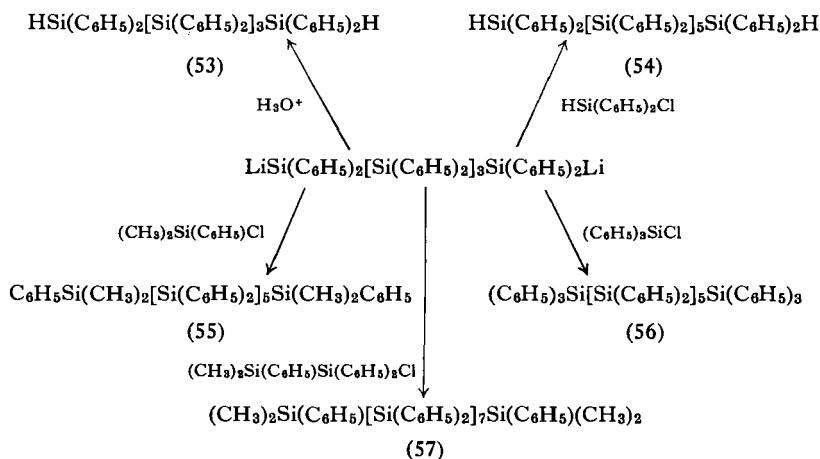
reaction which appears to be slow compared with lithium cleavage of decaphenylcyclopentasilane. Also, decaphenylcyclopentasilane has been shown to be relatively unreactive toward triphenylsilyllithium.⁹⁰ This accounts for the high yield of the primary cleavage product, which does not react further with decaphenylcyclopentasilane.

1,5-Dilithiodecaphenylpentasilane has also been subjected to acid hydrolysis, giving 1*H*,5*H*-decaphenylpentasilane (53),^{87, 91} and to reaction with a variety of chlorosilanes, with the view of providing pathways to silicon-functional polysilanes and to the preparation of longer chain silanes. Thus, chlorodiphenylsilane,^{41, 100} chlorodimethylphenylsilane,⁸⁷ chlorotriphenylsilane,^{49a} and 1-chloro-2,2-dimethyltriphenyldisilane^{90a} have reacted with 1,5-dilithiodecaphenylpentasilane to give the respective coupling products (54–57).

The dihydro compounds (53 and 54) were subsequently converted by phosphorus pentachloride¹⁰⁴ to 1,5-dichlorodecaphenylpentasilane and 1,7-dichlorotetradecaphenylheptasilane,⁸⁸ respectively.

Through the reaction of 1,5-dilithiodecaphenylpentasilane with dichlorodimethylsilane, another example of an organic substituted cyclosilane was realized. 1,1-Dimethyldecaphenylcyclohexasilane (10) is obtained in about 30% yield from this reaction.⁴¹ Attempts to prepare dodecaphenyl-

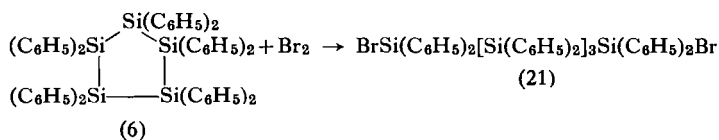
cyclohexasilane by treatment of the 1,5-dilithio compound with dichlorodiphenylsilane were inconclusive. From the reaction mixture octaphenylcyclotetrasilane (13%), decaphenylcyclopentasilane (25%), Compound "C" (2.4%), and a viscous, intractable oil were isolated.⁴¹ The yield of



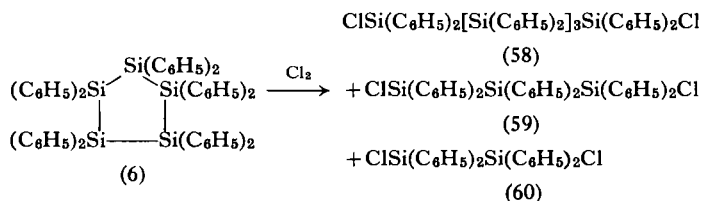
Compound "C" from this reaction is of the same order as that obtained from the direct preparation of the perphenylated cyclosilanes from dichlorodiphenylsilane and lithium in tetrahydrofuran, and, therefore, has little significance as to the structure of the compound.

B. With Halogens

Kipping reported that Compound "B" (decaphenylcyclopentasilane) reacted with bromine to give a mixture of products. These were subsequently hydrolyzed and a cyclic dioxide was isolated.¹³ This compound has more recently been shown to be octaphenyl-1,4-dioxacyclohexasilane.²⁹ It has been found that careful addition of an equivalent amount of bromine to decaphenylcyclopentasilane (6) in benzene results in a high yield of 1,5-dibromodecaphenylpentasilane (21).^{18, 38, 41} This dibromo compound was one of the important links in the chain of evidence leading to the correct structure of decaphenylcyclopentasilane.



Chlorine reacts with decaphenylcyclopentasilane with surprising ease to give 1,5-dichlorodecaphenylpentasilane (58), 1,3-dichlorohexaphenyltrisilane (59), and 1,2-dichlorotetraphenyldisilane (60), the quantity of each being determined by the reaction conditions.⁹⁵ Extended reaction times resulted in no isolable compounds, only viscous polymeric oils being formed.



A fairly extensive study of this reaction has been carried out and some of the results are listed in Table IV. It can be seen that increased reaction time and increased reaction temperature lead to more secondary cleavage products, and that benzene is a better solvent than carbon tetrachloride for

TABLE IV
REACTION OF DECAPHENYLCYCLOPENTASILANE WITH CHLORINE⁹⁵

Solvent ^a	Time (min.)	Temperature ^b (°C)	Starting material (%)	Dichloro derivatives ^{c, d} (%)		
				1,5-	1,3-	1,2-
Benzene	10	19 ± 1	32	87	—	—
Benzene	15	19 ± 1	Trace	76	—	—
Benzene	30	19 ± 1	0	33	—	10
Benzene	60	19 ± 1	0	—	—	—
Benzene	5	25–39	30	82	—	—
Benzene	15	25–46	0	30	42	4
CCl ₄	10	18–19	73	70	—	—
CCl ₄	30	21–25	8	50	—	—
CCl ₄	60	25–35	0	0	Trace	76
CCl ₄	4 hr	20–40	0	—	—	—

^a Reactions in benzene were carried out at the same chlorine gas flow rate.

^b In the first four reactions, the temperature was regulated by means of a Dry Ice-acetone bath; in all other runs, no attempt was made to regulate the temperature.

^c Based on unrecovered starting material.

^d The remainder of the reaction residue was a viscous oil from which no further products were isolated.

chlorination of decaphenylcyclopentasilane. Also, little or no 1,4-dichlorooctaphenyltetrasilane or dichlorodiphenylsilane was isolated⁹⁵ from these reactions. This result might have been expected from the fact that the rate of cleavage of alkylidisilanes containing chlorine atoms attached to silicon is significantly less than that of hexaalkylidisilanes.⁶⁶

Kipping reported that decaphenylcyclopentasilane is not cleaved by iodine under the conditions in which octaphenylcyclotetrasilane reacts rapidly.¹³ The relative reactivity of the halogens with decaphenylcyclopentasilane is $\text{Cl} > \text{Br} > \text{I}$, the same order observed in halogen cleavage of hexaalkylidisilanes.⁶⁶

C. With Other Halogenating Agents

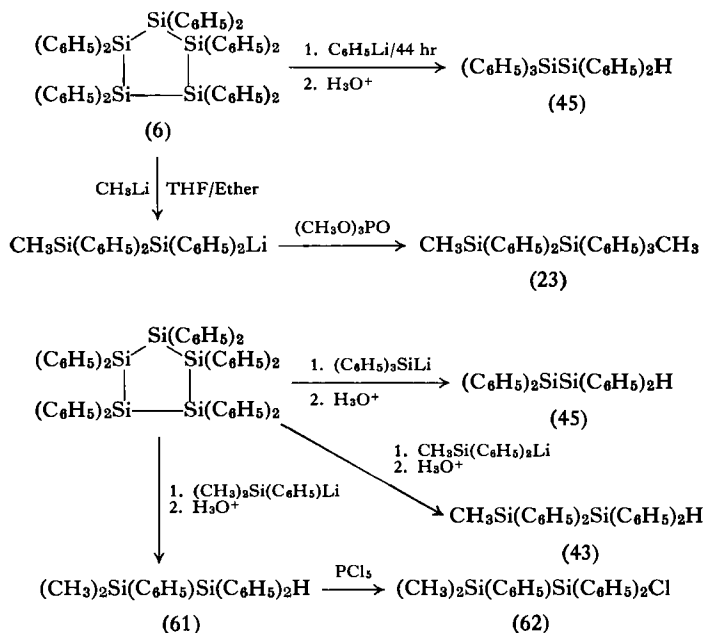
Phosphorus pentachloride can effect the chlorination of decaphenylcyclopentasilane, although not with the ease observed for octaphenylcyclotetrasilane.⁹⁵ When the reactants are refluxed in benzene or xylene, only recovered decaphenylcyclopentasilane has been obtained in high yield. However, in refluxing carbon tetrachloride or *sym*-tetrachloroethane, 1,5-dichlorodecaphenylpentasilane (58) is obtained in 13% and 72% yields, respectively.⁹⁵ Kipping observed that *sym*-tetrachloroethane did not react with decaphenylcyclopentasilane under conditions in which octaphenylcyclotetrasilane reacted readily, i.e., short reflux periods.¹³ However, it has been found that with extended reflux periods the cyclopentasilane undergoes cleavage to 1,5-dichlorodecaphenylpentasilane. For example, after 50 hours, 70% of the dichloro derivative (58) was isolated.⁹⁵

D. With Organometallic and Organosilylmetallic Reagents

Phenyllithium slowly cleaves decaphenylcyclopentasilane in tetrahydrofuran-ether to give, with an excess of organometallic compound and extended reaction times, pentaphenyldisilane (45)⁷⁰ as the major product after acid hydrolysis.⁹⁰ Decaphenylcyclopentasilane reacts with a 5 mole excess of methyllithium to give 1-lithio-2-methyltetraphenyldisilane, characterized as 1,2-dimethyltetraphenyldisilane (23).¹⁰²

Organosilyllithium compounds react, over extended periods, with decaphenylcyclopentasilane to give disilanyllithium compounds,⁹⁰ which have been used to prepare a variety of organic substituted disilanes. For example, triphenylsilyllithium reacts to give a 79% yield of pentaphenyldisilane (45) after acid hydrolysis.⁹⁰ Methylidiphenylsilyllithium¹⁸ and

dimethylphenylsilyllithium^{90a} have been used to cleave decaphenylcyclopentasilane to give 1*H*-2-methyltetraphenyldisilane (43) and 1*H*-2,2-dimethyltriphenyldisilane (61), respectively. The last-named compound was converted to the corresponding chlorosilane (62) with phosphorus pentachloride.^{90a}



VIII

REACTIONS OF COMPOUND "C"

Compound "C" is relatively unreactive in comparison with octaphenylcyclo-tetrasilane and decaphenylcyclopentasilane. Thus, it does not react with iodine, *sym*-tetrachloroethane, or refluxing nitrobenzene, nor does it react appreciably with alkali or aqueous piperidine.¹⁴

A. With Lithium Metal

Lithium reacts slowly with Compound "C" to give a mixture of dilithio compounds.⁴¹ The formation of derivatives of these mixtures with trimethyl

phosphate and with tri-*n*-butyl phosphate leads to 1,2- and 1,3-dialkyl compounds as the major products. The slowness of reaction might be attributed to a less reactive silicon-silicon bond; however, the insolubility of the compound in tetrahydrofuran is quite probably a contributing factor. Table V contains data concerning the lithium cleavage of Compound "C."

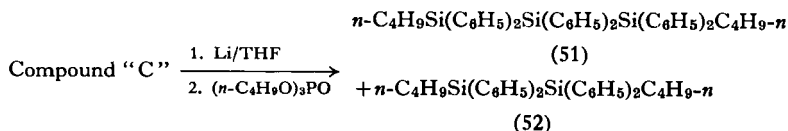


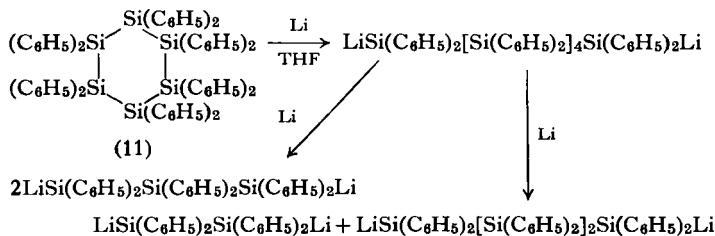
TABLE V

CLEAVAGE OF COMPOUND "C" BY LITHIUM IN TETRAHYDROFURAN⁴¹

Time (hr)	Temperature (°C)	Derivative made with	Recovered "C" (%)	Derivatives ^a (%)	
				1,3-	1,2-
5	25	(<i>n</i> -C ₄ H ₉ O) ₃ PO	42.0	41.5	4.5
8	25	(<i>n</i> -C ₄ H ₉ O) ₃ PO	11.4	39.3	13.4
13	65	(<i>n</i> -C ₄ H ₉ O) ₃ PO	5.7	28.7	21.7
14	25	(CH ₃ O) ₃ PO	5.0	55.6	14.9 ^b

^a Based on unrecovered "C".^b A trace of 1,4-dimethyloctaphenyltetrasilane was also isolated.

If Compound "C" is dodecaphenylcyclohexasilane (11), then the cleavage with lithium may be represented as in the reaction scheme below. The 1,6-dilithiododecaphenylhexasilane might be expected to undergo further cleavage with lithium to give 1,3-dilithiohexaphenyltrisilane. A less favorable cleavage would give 1,2-dilithiotetraphenylidisilane and 1,4-dilithio-octaphenyltetrasilane.



B. With Halogens

Compound "C" does not react with iodine nor does it add bromine in refluxing benzene.⁴¹ Under the same conditions, chlorine also does not react; however, when refluxing *o*-dichlorobenzene is used as the solvent, cleavage is complete within 5 minutes. The reaction products consist of a mixture of dichloropolysilanes and viscous polymers from which no materials of greater chain length than tetrasilanes could be isolated. Similar results were obtained from the extended reaction of phosphorus pentachloride with Compound "C" in refluxing *sym*-tetrachloroethane.⁴¹ Compound "C" was also found to be unreactive with mercuric chloride in refluxing benzene or tetrahydrofuran.⁴¹

C. With Organometallic Reagents

In contrast to octaphenylcyclotetrasilane and decaphenylcyclopentasilane, Compound "C" is resistant to methyllithium cleavage.⁴¹ Benzyl-lithium, which is known to cause rapid cleavage of hexaphenyldisilane,¹⁰⁵ reacts only very slowly with "C." The only product isolated from this reaction, other than recovered Compound "C," was diphenylsilanediol (12).⁴¹ Research is still in progress on the structure of Compound "C."

IX

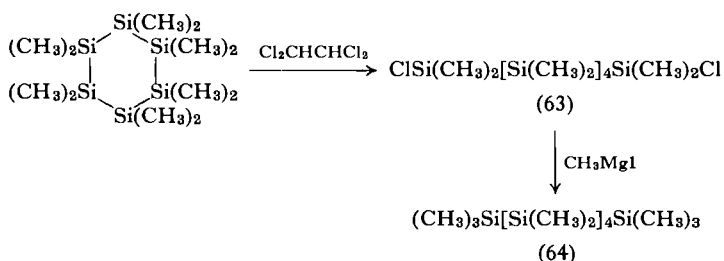
REACTIONS OF DODECAMETHYLCYCLOHEXASILANE

The intensive study of the reactions of the organic substituted cyclosilane, dodecamethylcyclohexasilane, has only recently begun.^{49, 105a} However, to be as complete as possible in discussing the chemistry of cyclosilanes, a few reactions of this compound will be discussed with the reservation that the results presented are, at this point, tentative.

A. With Halogenating Agents

Mercuric chloride in refluxing tetrahydrofuran (THF) cleaves dodecamethylcyclohexasilane to give a mixture of dichlorosilanes, with evidence for compounds containing one, two, and three silicon atoms.⁴⁹ Dodecamethylcyclohexasilane also undergoes halogenation by refluxing *sym*-tetrachloroethane to give as the major product (*ca.* 40%) a compound which is

apparently 1,6-dichlorododecamethylhexasilane (63). Indications are that other shorter chain silanes are also produced. The 1,6-dichloro compound (63) reacted with methylmagnesium iodide to give the corresponding tetradecamethylhexasilane (64).⁴⁹ Vapor phase chromatography indicated this compound (64) to be slightly impure. Infrared analysis showed the presence of siloxane-containing material.



B. With Organometallic Reagents

Excess methyllithium reacted with dodecamethylcyclohexasilane in a mixture of tetrahydrofuran and ether evidently in a manner similar to that observed with the phenylated cyclic compounds. Subsequent to treatment of the reaction mixture with chlorotrimethylsilane, there was obtained a complex mixture of products. Judging from their boiling points, the products were composed of permethylated polysilanes containing three to seven or eight silicon atoms.⁴⁹ Only decamethyltetrasilane^{106, 106a} and dodecamethylpentasilane were isolated in a relatively pure state.

X

ORGANOPOLYSILANES

Many organic substituted compounds containing the silicon-silicon bond are known.^{1, 107} The majority of these compounds are disilanes. However, as can be seen in the information presented in this chapter, highly phenylated organopolysilanes with definite chain lengths of at least nine silicon atoms are capable of existence. It would appear that chain length is not a limiting factor in the stability of these compounds. All of the compounds isolated are stable to spontaneous decomposition, and the majority of them are also

stable at their melting points. The reason for the paucity of organic substituted polysilanes appears then to be a lack of synthetic methods, rather than a lack of stability of such compounds.

In order to provide a convenient catalog of the compounds isolated and referred to in this chapter, Table VI lists these compounds, their melting point or boiling point, and appropriate references.

TABLE VI
ORGANOPOLYSILANES

Formula	Name	M.p. (b.p.) (° C)	Reference
<i>Disilanes</i>			
C ₄ H ₁₂ Cl ₂ Si ₂	1,2-Dichlorotetramethyldisilane	(148)	(68)
C ₆ H ₁₈ Si ₂	Hexamethyldisilane	14–14.4	(1)
C ₂₀ H ₂₁ ClSi ₂	1-Chloro-2,2-dimethyltriphenyldisilane	(157/0.005 mm)	(90a)
C ₂₀ H ₂₂ Si ₂	1 <i>H</i> -2,2-dimethyltriphenyldisilane	(126–7/0.002 mm)	(90a)
C ₂₄ H ₂₀ Br ₂ Si ₂	1,2-Dibromotetraphenyldisilane	154.5–155.5	(26)
C ₂₄ H ₂₀ Cl ₂ Si ₂	1,2-Dichlorotetraphenyldisilane	114.5–115	(26)
C ₂₄ H ₂₁ ClSi ₂	1 <i>H</i> -2-Chlorotetraphenyldisilane	45–50	(49)
C ₂₄ H ₂₂ Si ₂	1 <i>H</i> ,2 <i>H</i> -Tetraphenyldisilane	79–80	(26, 86)
C ₂₄ H ₂₂ O ₂ Si ₂	Tetraphenyldisilane-1,2-diol	139–140	(26)
C ₂₅ H ₂₄ Si ₂	1 <i>H</i> -2-Methyltetraphenyldisilane	71–73	(18)
C ₂₆ H ₂₆ Si ₂	1,2-Dimethyltetraphenyldisilane	141–143	(86)
C ₃₀ H ₂₅ ClSi ₂	1-Chloropentaphenyldisilane	154–155	(52)
C ₃₀ H ₂₆ OSi ₂	Pentaphenyldisilane-1-ol	134–134.5	(67)
C ₃₀ H ₂₆ Si ₂	1 <i>H</i> -Pentaphenyldisilane	128–129	(67)
C ₃₂ H ₃₈ Si ₂	1,2-Di- <i>n</i> -butyltetraphenyldisilane	101–102	(41)
C ₃₆ H ₃₀ Si ₂	Hexaphenyldisilane	368–370	(55)
<i>Trisilanes</i>			
C ₈ H ₂₄ Si ₃	Octamethyltrisilane	(180, n_D^{20} 1.4599)	(106)
C ₃₆ H ₃₀ Cl ₂ Si ₃	1,3-Dichlorohexaphenyltrisilane	128.5–131	(104)
C ₃₆ H ₃₂ O ₂ Si ₃	Hexaphenyltrisilane-1,3-diol	146.5–148	(38)
C ₃₆ H ₃₂ Si ₃	1 <i>H</i> ,3 <i>H</i> -Hexaphenyltrisilane	97–98	(38)
C ₃₇ H ₃₃ ClSi ₃	1-Chloro-3-methylhexaphenyltrisilane	88–90	(104)
C ₃₇ H ₃₄ Si ₃	1 <i>H</i> -3-Methylhexaphenyltrisilane	96–97	(102)
C ₃₈ H ₃₆ Si ₃	1,3-Dimethylhexaphenyltrisilane	92–93	(102)
C ₃₈ H ₃₆ Si ₃	2,2-Dimethylhexaphenyltrisilane	223–227	(49)
C ₄₄ H ₄₈ Si ₃	1,3-Di- <i>n</i> -butylhexaphenyltrisilane	147.5–149	(41)
C ₄₈ H ₄₀ Si ₃	Octaphenyltrisilane	260–262	(52)

Continued.

TABLE VI (continued).

Formula	Name	M.p. (b.p.) (° C)	Reference
<i>Tetrasilanes</i>			
C ₁₀ H ₃₀ Si ₄	Decamethyltetrasilane	(242, n_D^{20} 1.4876)	(106)
C ₄₈ H ₄₀ Br ₂ Si ₄	1,4-Dibromooctaphenyltetrasilane	220–221	(92)
C ₄₈ H ₄₀ Cl ₂ Si ₄	1,4-Dichlorooctaphenyltetrasilane	185–186	(13, 17)
C ₄₈ H ₄₀ I ₂ Si ₄	1,4-Diiodooctaphenyltetrasilane	274–276	(13, 17)
C ₄₈ H ₄₀ Si ₄	Octaphenylcyclotetrasilane	313–316 dec.	(13, 17, 35)
C ₄₈ H ₄₀ OSi ₄	Octaphenyloxacyclopentasilane	226–228	(13, 29)
		234–236	(29)
C ₄₈ H ₄₀ O ₂ Si ₄	Octaphenyl-1,3-dioxacyclohexasilane ^a	245–246	(13, 29)
C ₄₈ H ₄₀ O ₂ Si ₄	Octaphenyl-1,4-dioxacyclohexasilane	219–220	(29)
C ₄₈ H ₄₁ BrSi ₄	1 <i>H</i> -4-Bromooctaphenyltetrasilane	166–167	(94)
C ₄₈ H ₄₁ ClSi ₄	1 <i>H</i> -4-Chlorooctaphenyltetrasilane	162–163	(94)
C ₄₈ H ₄₂ OSi ₄	4 <i>H</i> -Octaphenyltetrasilane-1-ol	181–183	(94)
C ₄₈ H ₄₂ O ₂ Si ₄	Octaphenyltetrasilane-1,4-diol	212–214	(38)
C ₄₈ H ₄₂ Si ₄	1 <i>H</i> ,4 <i>H</i> -Octaphenyltetrasilane	160–162	(34)
C ₄₉ H ₄₃ ClSi ₄	1-Chloro-4-methyloctaphenyltetrasilane	200–201	(104)
C ₄₉ H ₄₄ Si ₄	1 <i>H</i> -4-Methyloctaphenyltetrasilane	218–220	(102)
C ₅₀ H ₄₆ Si ₄	1,4-Dimethyloctaphenyltetrasilane	220–222	(17)
C ₅₂ H ₄₆ O ₄ Si ₄	1,4-Diacetoxyoctaphenyltetrasilane	233–235	(101)
C ₅₂ H ₅₀ Si ₄	1,4-Diethyloctaphenyltetrasilane	253–254	(27)
C ₅₆ H ₅₆ Si ₄	Octa- <i>p</i> -tolylcyclotetrasilane	290–293 dec.	(15)
C ₅₆ H ₅₆ I ₂ Si ₄	1,4-Diiodoocta- <i>p</i> -tolyltetrasilane	300 dec.	(15)
C ₅₆ H ₅₆ OSi ₄	Octa- <i>p</i> -tolylloxacyclopentasilane	228–229	(15)
C ₅₆ H ₅₈ Si ₄	1,4-Di- <i>n</i> -butyloctaphenyltetrasilane	217–218	(41)
C ₆₀ H ₅₀ Si ₄	Decaphenyltetrasilane	358–360	(17)
C ₆₈ H ₈₂ Si ₄	1,4-Di- <i>n</i> -decyloctaphenyltetrasilane	70–71	(41)
<i>Pentasilanes</i>			
C ₁₂ H ₃₆ Si ₅	Dodecamethylpentasilane ^a	(75–78/0.11 mm, n_D^{20} 1.5082)	(49a)
C ₆₀ H ₅₀ Br ₂ Si ₅	1,5-Dibromodecaphenylpentasilane	205–207	(18, 41)
C ₆₀ H ₅₀ Cl ₂ Si ₅	1,5-Dichlorodecaphenylpentasilane	179–180	(95)
C ₆₀ H ₅₀ Si ₅	Decaphenylcyclopentasilane	440–444	(13, 18)
		466–470	(19, 41)
C ₆₀ H ₅₂ O ₂ Si ₅	Decaphenylpentasilane-1,5-diol	169–170	(18, 38)
C ₆₀ H ₅₂ Si ₅	1 <i>H</i> ,5 <i>H</i> -decaphenylpentasilane	147–148	(87, 91)
C ₆₂ H ₅₆ Si ₅	1,5-Dimethyldecaphenylpentasilane	181–182	(18, 41)
C ₆₆ H ₆₄ O ₂ Si ₅	1,5-Di- <i>n</i> -propoxydecaphenylpentasilane	195–196	(95)
C ₆₈ H ₆₈ Si ₅	1,5-Di- <i>n</i> -butyldecaphenylpentasilane	162–164	(41)
C ₇₀ H ₇₀ Si ₅	Deca- <i>p</i> -tolylcyclopentasilane	310	(31)

Continued.

TABLE VI (continued).

Formula	Name	M.p. (b.p.) (° C)	Reference
<i>Hexasilanes</i>			
C ₁₂ H ₃₆ Si ₆	Dodecamethylcyclohexasilane	250–252	(16)
C ₁₂ H ₃₆ Cl ₂ Si ₆	1,6-Dichlorododecamethylhexasilane	(137–144/0.6 mm)	(49a)
C ₁₄ H ₄₂ Si ₆	Tetradecamethylhexasilane	(115–116/0.4 mm, n_D^{20} 1.5180)	(49a)
C ₅₄ H ₅₆ Si ₆	1,1,1,6,6,6-Hexamethyloctaphenylhexasilane	295–297	(34)
C ₆₂ H ₅₆ Si ₆	1,1-Dimethyldecaphenylcyclohexasilane	472–476	(41)
C ₇₂ H ₆₀ Cl ₂ Si ₆	1,6-Dichlorododecaphenylhexasilane	237–239	(100)
C ₇₂ H ₆₀ Si ₆	Dodecaphenylcyclohexasilane ^a	502–504 dec.	(41)
C ₇₂ H ₆₂ Si ₆	1 <i>H</i> ,6 <i>H</i> -Dodecaphenylhexasilane	186–188	(100)
C ₇₄ H ₆₆ Si ₆	1,6-Dimethyldodecaphenylhexasilane	209–211	(100)
<i>Heptasilanes</i>			
C ₆₆ H ₆₈ Si ₇	1,1,1,7,7,7-Hexamethyldecaphenylheptasilane	197–199	(41)
C ₇₆ H ₇₂ Si ₇	1,1,7,7-Tetramethyldodecaphenylheptasilane	211–214	(87)
C ₈₄ H ₇₀ Cl ₂ Si ₇	1,7-Dichlorotetradecaphenylheptasilane	209–211	(100)
C ₈₄ H ₇₂ Si ₇	1 <i>H</i> ,7 <i>H</i> -Tetradecaphenylheptasilane	203–204	(41)
C ₈₆ H ₇₆ Si ₇	1,7-Dimethyltetradecaphenylheptasilane	215–217	(100)
C ₉₆ H ₈₀ Si ₇	Hexadecaphenylheptasilane	296–298	(49a)
<i>Nonasilanes</i>			
C ₁₀₀ H ₉₂ Si ₉	1,1,9,9-Tetramethylhexadecaphenylnonasilane	230–232	(90a)

^a Tentative structures.

XI

SUMMARY AND CONCLUSIONS

Representative organic substituted cyclosilanes, as illustrated by octaphenylcyclotetrasilane (5), decaphenylcyclopentasilane (6), and their *p*-tolyl analogs (7 and 8), and dodecamethylcyclohexasilane (9), have been characterized and shown to undergo reactions which are generally common to compounds containing the disilane linkage. The relative reactivities of these cyclosilanes has been attributed mainly to steric factors and substituent

groups on silicon, with the consideration that the silicon atom involved in reaction can attain a pentavalent state.

The extreme reactivity of octaphenylcyclotetrasilane with a variety of reagents, some of which are not ordinarily considered capable of silicon-silicon bond cleavage, had previously been described as being due to the presence of a silyl radical species²⁸ or to ring strain which is then responsible for homolytic scission of the silicon-silicon bond.¹⁷ It has been proposed here that homolytic cleavage is not necessarily important in the reactions of octaphenylcyclotetrasilane, but that the molecular geometry of the compound greatly facilitates the formation of a pentavalent complex which undergoes easy cleavage to give the observed products.

Dodecaphenylcyclohexasilane has been the structure considered for Kipping's Compound "C";¹⁴ however, the exact structure proof has not as yet been accomplished. The unreactivity of this compound is, however, probably best ascribed to the structure considered.

The products of reactions of the cyclosilanes are organic-substituted polysilanes, which can be considered to be the shorter chain members of a new class of compounds. Further research into the preparation and chemical behavior of such materials is necessary to establish more firmly the structures of these compounds and an explanation of their special properties.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of William H. Atwell, Frank K. Cartledge, and Drs. Robert K. Ingham, Ann W. P. Jarvie, Glen Lichtenwalter, Richard A. Tomasi, Hans J. S. Winkler, and Ernest A. Zuech. Some of the research was supported in part by the United States Air Force under Contracts AF33(616)-3510 and 6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

REFERENCES

1. See C. Eaborn, "Organosilicon Compounds," pp. 86-117. Butterworths, London, 1960, for a more complete discussion of these topics.
2. A. Stock, "Hydrides of Boron and Silicon," pp. 20-37. Cornell Univ. Press, Ithaca, New York, 1933.
3. K. Borer and C. S. G. Phillips, *Proc. Chem. Soc.* p. 189 (1959).
4. R. Schwarz and H. Meckbach, *Z. Anorg. Allgem. Chem.* **232**, 241 (1937); R. Schwarz and R. Thiel, *ibid.* **235**, 247 (1938).
5. F. G. A. Stone, "Hydrogen Compounds of Group IV Elements." Prentice-Hall, Englewood Cliffs, New Jersey, 1962.

- 6a. G. E. Coates, "Organometallic Compounds," 2nd ed., pp. 174, 197. Wiley, New York, 1960.
- 6b. W. P. Neumann, *Angew. Chem.* **74**, 122 (1962); W. P. Neumann and K. König, *ibid.* **74**, 215 (1962).
- 6c. W. P. Neumann, *Angew. Chem.* **75**, 679 (1963).
7. See G. Schott, *Z. Chem.* **2**, 194 (1962) and pertinent references cited therein.
8. For two somewhat different interpretations, see C. Eaborn, "Organosilicon Compounds," pp. 113-114. Butterworths, London, 1960; C. A. Coulson, "Valence," 2nd ed., pp. 184-188. Oxford Univ. Press, London and New York, 1961.
9. F. Pass and H. Schindlbauer, *Monatsh. Chem.* **90**, 148 (1959).
10. J. H. Burns and J. Waser, *J. Am. Chem. Soc.* **79**, 859 (1957).
11. R. Schwarz and F. Heinrich, *Z. Anorg. Allgem. Chem.* **221**, 276 (1935).
12. A. Stock and C. Somieski, *Ber. Deut. Chem. Ges.* **56B**, 132 (1923).
13. F. S. Kipping and J. E. Sands, *J. Chem. Soc.* **119**, 830 (1921).
14. F. S. Kipping, *J. Chem. Soc.* **125**, 2291 (1924).
15. A. R. Steele and F. S. Kipping, *J. Chem. Soc.* p. 2545 (1929).
16. C. A. Burkhard, *J. Am. Chem. Soc.* **71**, 963 (1949).
17. A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.* **83**, 1921 (1961).
18. H. J. S. Winkler, A. W. P. Jarvie, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.* **83**, 4089 (1961).
19. H. Gilman, unpublished studies presented before the American Chemical Society, 141st National Meeting, 1962.
- 19a. E. Hengge, H. Reuter, and R. Petzold, *Angew. Chem.* **75**, 677 (1963).
20. Commission of Nomenclature of Organic Chemistry, *Compt. Rend. Conf. Union Intern. Chim. Pure Appl. 15th Amsterdam 1949* pp. 127-132 (1949).
21. American Chemical Society Official Reports, *Chem. Eng. News* **30**, 4517-4522 (1952).
22. F. S. Kipping, *Proc. Chem. Soc.* **27**, 143 (1911).
23. F. S. Kipping, *J. Chem. Soc.* p. 2719 (1927).
24. F. S. Kipping, *J. Chem. Soc.* p. 2728 (1927).
25. F. S. Kipping and J. E. Sands, *J. Chem. Soc.* **119**, 848 (1921).
26. H. J. S. Winkler and H. Gilman, *J. Org. Chem.* **26**, 1265 (1961).
27. F. S. Kipping, *J. Chem. Soc.* **123**, 2598 (1923).
28. F. S. Kipping, *J. Chem. Soc.* **123**, 2590 (1923).
29. A. W. P. Jarvie, H. J. S. Winkler, and H. Gilman, *J. Org. Chem.* **27**, 614 (1962).
30. W. Schlenk and H. Mark, *Ber. Deut. Chem. Ges.* **55B**, 2285 (1922).
31. When the reaction was carried out in xylene no crystalline compounds could be isolated.¹⁵
32. F. S. Kipping, *Proc. Roy. Soc.* **A159**, 139 (1937).
33. See H. Gilman and H. J. S. Winkler, in "Organometallic Chemistry" (H. Zeiss, ed.), pp. 270-345. Reinhold, New York, 1960, for a comprehensive review of silylmetallic compounds. See also, D. Wittenberg and H. Gilman, *Quart. Rev. (London)* **13**, 116 (1959). Well before that time, a question arose on the existence of tervalent silicon. A wide variety of studies was carried out on the possibility of dissociation of hexaaryldisilanes to triarylsilyl units. See H. Gilman and G. E. Dunn, *Chem. Rev.* **52**, 77 (1953); H. Gilman and T. C. Wu, *J. Am. Chem. Soc.* **75**, 3762 (1953); H. Gilman and T. C. Wu, *J. Org. Chem.* **23**, 913 (1958), as well as other related publications.

34. H. Gilman and D. J. Peterson, unpublished studies.
35. H. Gilman, D. J. Peterson, A. W. P. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.* **82**, 2076 (1960). J. H. Chaudet and Dr. W. D. Kennedy of the Tennessee Eastman Company performed the electron paramagnetic resonance measurements.
36. G. A. Razuvaev, N. S. Vyazankin, and Y. I. Dergunov, *Zh. Obshch. Khim.* **30**, 1310 (1960).
37. F. S. Kipping, *J. Chem. Soc.* **101**, 2113 (1912).
38. G. R. Chainani, S. Cooper, and H. Gilman, *J. Org. Chem.* **28**, 2146 (1963).
39. A. W. P. Jarvie and H. Gilman, *Chem. Ind. (London)* p. 1271 (1960).
40. Mechrolab, Inc., Mountain View, California.
41. H. Gilman and G. L. Schwebke, unpublished studies.
42. C. A. Glover and R. R. Stanley, *Anal. Chem.* **33**, 447 (1961).
43. Determined by Dr. C. A. Glover, Tennessee Eastman Company Research Laboratories. See H. Gilman and G. L. Schwebke, *J. Am. Chem. Soc.* **85**, 1016 (1963).
44. Determined by Dr. H. W. Patton, Tennessee Eastman Company Research Laboratories. See H. Gilman and G. L. Schwebke, *J. Am. Chem. Soc.* **85**, 1016 (1963).
45. S. L. Liu and H. Gilman, unpublished studies.
46. L. A. Harrah, M. T. Ryan, and C. Tamborski, *Spectrochim. Acta* **18**, 21 (1962).
- 46a. O. M. Nefedov, M. N. Manakov and A. D. Petrov, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk* p. 1717 (1961); *Chem. Abstr.* **56**, 3507 (1962).
47. Dodecamethylcyclohexasilane was described as being hydrocarbon soluble and subliming above 100° with a transition temperature of 74°. ¹⁶ Recently, this compound has been prepared, again in low yield, from lithium and dichlorodimethylsilane in tetrahydrofuran under conditions similar to those of Burkhard¹⁶; E. Hengge and H. Reuter, *Naturwissenschaften* **49**, 514 (1962).
48. R. P. Anderson, private communication.
49. H. Gilman and R. A. Tomasi, *J. Org. Chem.* **28**, 1651 (1963).
- 49a. H. Gilman and R. A. Tomasi, unpublished studies.
50. H. Gilman and T. C. Wu, *J. Am. Chem. Soc.* **73**, 4031 (1951).
51. D. Wittenberg and H. Gilman, *Quart. Rev. (London)* **13**, 116 (1959).
52. H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, and S. H. Eidt, *J. Am. Chem. Soc.* **74**, 561 (1952).
53. H. Gilman and T. C. Wu, *J. Org. Chem.* **18**, 753 (1953).
54. H. Gilman, R. K. Ingham, and A. G. Smith, *J. Org. Chem.* **18**, 1743 (1953).
55. H. Gilman and T. C. Wu, *J. Am. Chem. Soc.* **75**, 3762 (1953).
56. H. Gilman, G. D. Lichtenwalter, and D. Wittenberg, *J. Am. Chem. Soc.* **81**, 5320 (1959).
57. A. G. Brook and H. Gilman, *J. Am. Chem. Soc.* **76**, 278 (1954).
58. H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.* **80**, 608 (1958).
59. H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. Ind. (London)* p. 1479 (1958).
60. H. Gilman and W. Steudel, *Chem. Ind. (London)* p. 1094 (1959).
61. H. Gilman, R. A. Klein, and H. J. S. Winkler, *J. Org. Chem.* **26**, 2474 (1961).
62. See H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.* **24**, 1588 (1959) and pertinent references cited therein.
63. B. J. Gaj and H. Gilman, *Chem. Ind. (London)* p. 493 (1960).
64. H. Gilman, G. D. Lichtenwalter, and D. Wittenberg, *J. Am. Chem. Soc.* **81**, 5320 (1959).
65. G. Martin, *J. Chem. Soc.* **107**, 1043 (1915).
66. G. Schott and C. Harzdorf, *Z. Anorg. Allgem. Chem.* **306**, 180 (1960); **307**, 105 (1961).

67. H. Gilman and J. J. Goodman, *J. Am. Chem. Soc.* **75**, 1250 (1953).
68. A. Taketa, M. Kumada, and K. Tarama, *Nippon Kagaku Zasshi* **78**, 999 (1957); *Chem. Abstr.* **52**, 8942 (1958).
69. F. S. Kipping, *J. Chem. Soc.* **119**, 647 (1921).
70. H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.* **73**, 5077 (1958).
71. T. C. Wu and H. Gilman, *J. Org. Chem.* **23**, 913 (1958).
72. M. Kumada, J. Nakajima, M. Ishikawa, and Y. Yamamoto, *J. Org. Chem.* **23**, 292 (1958); M. Kumada, K. Shiina, and M. Yamaguchi, *J. Chem. Soc. Japan Ind. Chem. Sect.* **57**, 230 (1954); *Chem. Abstr.* **49**, 11542 (1955).
73. W. Schlenk, J. Ranning, and G. Racky, *Ber. Deut. Chem. Ges.* **44**, 1178 (1911).
74. A. J. Petro and C. P. Smyth, *J. Am. Chem. Soc.* **79**, 6147 (1957).
75. However, recent evidence indicates that the dissociation energy of the silicon-silicon bond of disilane is 81.3 kcal mole⁻¹, comparable to the dissociation energy of the carbon-carbon bond in ethane (83 kcal mole⁻¹), rather than earlier values of about 50 kcal mole⁻¹; W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.* **84**, 3599 (1962).
76. For discussions of strain theory concerning carbon compounds and its theoretical implications, see W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. 1. Elsevier, Amsterdam, 1955; J. Sicher, *Progr. Stereochem.* **3**, 202-263 (1962).
77. M. K. Wilson and S. M. Polo, cited in reference 79.
78. L. H. Sommer and G. A. Baum, *J. Am. Chem. Soc.* **76**, 5002 (1954).
79. R. West, *J. Am. Chem. Soc.* **77**, 2339 (1955).
80. W. H. Knoch, Jr., and R. V. Lindsey, Jr., *J. Org. Chem.* **23**, 1392 (1958).
81. L. H. Sommer, O. F. Bennet, P. G. Campbell, and D. R. Weyenberg, *J. Am. Chem. Soc.* **79**, 3295 (1957).
82. The rate of hydrolysis of 1-methylsilacyclobutane (30) to the corresponding silanol (31) is 10⁴-10⁵ times faster than the hydrolysis of triethylsilane to triethylsilanol.⁸¹
83. The concept of internal strain (I-strain) of cyclic compounds [cf. H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.* **73**, 212 (1951)] appears to have been replaced in some cases with that of a change of orbital hybridization to compensate for geometrical requirements brought about by ring formation. See, Sister M. Brandon, M. Tamres, and S. Searles, Jr., *J. Am. Chem. Soc.* **82**, 2129 (1960); D. E. McLaughlin, M. Tamres, and S. Searles, Jr., *ibid.* p. 5621.
84. H. Gilman and J. M. Kraemer, unpublished studies.
85. H. Gilman and H. J. S. Winkler, unpublished studies.
86. W. Steudel and H. Gilman, *J. Am. Chem. Soc.* **82**, 6129 (1960).
87. H. Gilman and S. Cooper, unpublished studies.
88. H. Gilman, S. Cooper, and R. Harrell, unpublished studies.
89. H. Gilman, G. L. Schwebke, and K. Y. Chang, unpublished studies.
90. A. W. P. Jarvie and H. Gilman, *J. Org. Chem.* **26**, 1999 (1961).
- 90a. H. Gilman and R. A. Tomasi, *Chem. Ind. (London)* p. 954 (1963).
91. H. J. S. Winkler and H. Gilman, *J. Org. Chem.* **27**, 254 (1962).
92. H. Gilman, J. M. Kraemer, W. H. Atwell, and G. L. Schwebke, unpublished studies.
93. H. Gilman and A. W. P. Jarvie, *Chem. Ind. (London)* p. 965 (1960).
94. H. Gilman, D. R. Chapman, and G. L. Schwebke, unpublished studies.
95. H. Gilman and D. R. Chapman, unpublished studies.
96. H. Gilman and R. A. Tomasi, *J. Org. Chem.* **27**, 3647 (1962).
97. R. Connor, K. Folkers, and H. Adkins, *J. Am. Chem. Soc.* **54**, 1138 (1932).
98. F. S. Kipping and A. G. Murray, *J. Chem. Soc.* p. 360 (1929).
99. H. Gilman and B. J. Gaj, *J. Org. Chem.* **26**, 247 (1961).

100. H. Gilman and R. Harrell, unpublished studies.
101. H. Gilman and W. H. Atwell, unpublished studies.
102. H. Gilman and K. Y. Chang, unpublished studies.
103. H. Gilman, F. K. Cartledge, and S. Y. Sim, unpublished studies.
104. S. Cooper, G. R. Chainani, R. A. Tomasi, K. Y. Chang, and H. Gilman, unpublished studies.
105. H. Gilman and G. L. Schwebke, *J. Org. Chem.* **27**, 4259 (1962).
- 105a. U. G. zu Stolberg, *Angew. Chem.* **75**, 206 (1963).
106. U. G. zu Stolberg, *Angew. Chem.* **74**, 696 (1962).
- 106a. G. R. Wilson and A. G. Smith, *J. Org. Chem.* **26**, 557 (1961).
107. A recent review treating organopolysilanes has been published, D. Dabrowska and A. Radecki, *Wiadomosci Chem.* **16**, 361 (1962); *Chem. Abstr.* **58**, 4593 (1963).

Fluorocarbon Derivatives of Metals

P. M. TREICHEL¹ and F. G. A. STONE²

*Department of Chemistry, Queen Mary College
University of London, London*

I. Introduction	143
II. Lithium Derivatives	145
III. Magnesium Derivatives	150
IV. Derivatives of Group IIIb Elements	153
A. Boron	153
B. Aluminum	159
V. Derivatives of Group IVb Elements	161
A. Silicon	161
B. Germanium	165
C. Tin	166
D. Lead	174
VI. Transition Metal Derivatives	174
A. Introduction	174
B. Perfluoroalkyl, Polyfluoroalkyl, Perfluoroalkenyl, and Pentafluoro- phenyl Compounds	178
C. Fluorocarbon π Complexes	195
VII. Derivatives of Group IIb Elements	200
A. Zinc and Cadmium	200
B. Mercury	201
VIII. Spectroscopic Studies	206
A. Nuclear Magnetic Resonance Spectroscopy	206
B. Infrared Spectra	212
References	216

I

INTRODUCTION

It is the purpose of this article to review the chemistry of fluorocarbon derivatives of metals. At present the great majority of these compounds are those in which a metal is bonded to a carbon atom which is in turn linked to

¹ Present address, Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

² Present address: Department of Inorganic Chemistry, The University, Bristol, England.

one or more fluorine atoms. Very recently, however, several organometallic compounds have been reported, for example pentafluorophenylmagnesium bromide and transition metal complexes of perfluorobut-2-yne, which do not fall within this definition, but nevertheless should also be regarded as fluorocarbon derivatives of metals.

Studies in this rapidly expanding area of endeavor began about fifteen years ago. Following the discovery of perfluoroalkyl iodides, notably CF_3I , perfluoroalkylmercurials were isolated by Emeléus and Haszeldine and their co-workers (1-4).³ Concurrently, some evidence was obtained for the formation of perfluoroalkyllithium and perfluoroalkyl Grignard reagents. This work was particularly valuable, indicating strongly that fluorocarbon derivatives of metals would possess a distinctly different chemistry from that of their hydrocarbon analogs. For example, the compound $(\text{CF}_3)_2\text{Hg}$ proved to be a white crystalline solid, water soluble but affording fluoroform on treatment with alkali. In contrast and as is well known, dimethylmercury is a liquid. Furthermore, it is insoluble in water and hydrolytically stable under conditions which lead to the decomposition of bis(perfluoromethyl)mercury. In spite of observations such as these, the field of fluorocarbon derivatives of the metals, except for mercury, remained largely undeveloped. This situation arose primarily through lack of suitable methods of synthesis, whereas following early work on perfluoroalkyl iodides it had proved fairly easy to prepare numerous polyfluoroalkyl derivatives of nonmetals and metalloids by such direct reactions as those between the element and perfluoroalkyl iodides. Consequently, knowledge of fluorocarbon compounds of nonmetals and metalloids has been developed extensively, and much is now known about their chemical and physical properties. This aspect of fluorine chemistry has been the subject of two recent reviews (5, 5a).

As a result of the efforts of many chemists during the last two or three years fluorocarbon derivatives of metals have been described in ever increasing numbers, so that it can now be reasonably said that their study forms an important subarea both of fluorine chemistry and of organometallic chemistry. As anticipated by the early work (1-4), the new compounds display novel properties and reactions in comparison with those of their hydrocarbon

³ The term perfluoroalkyl, abbreviated R_F , will be used to designate an alkyl group in which all hydrogen atoms are replaced by fluorine atoms. Alkyl groups containing a high proportion of fluorine (e.g. HCF_2CF_2-) will be called polyfluoroalkyl. The $\text{CF}_2:\text{CF}$ group will be referred to as the perfluorovinyl rather than the trifluorovinyl group, and C_6F_5 as the pentafluorophenyl group.

analogous, thereby adding greatly to our knowledge of organometallic chemistry, fluorine chemistry, and the nature of chemical bonding. These novel properties and reactions are in accord with the well-known propensity of fluorine for stabilizing new structures and oxidation states. It now appears likely that increasing numbers of organometallics containing a high percentage of fluorine will be isolated.

In this review compounds of metals of the main groups are discussed systematically according to the Periodic Table, and this is followed by a survey of fluorocarbon derivatives of the transition metals and the zinc subgroup. Compounds of boron and silicon will be considered even though these elements are not metals in the real sense of the term. Nevertheless, studies on fluorocarbon derivatives of boron and silicon established important principles applicable to fluorocarbon-metal compounds in general, and, moreover, surveys of organometallic chemistry customarily discuss boron and silicon compounds. Compounds of the heavier Group V elements are not reviewed, principally because of the availability of fairly up to date surveys (5, 5a). The review is concluded with some remarks about spectroscopic studies.

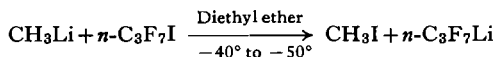
II

LITHIUM DERIVATIVES

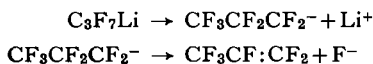
In view of the significant role played by organolithium and organomagnesium compounds in the synthesis of organometallics in general, it might have been expected that polyfluoroalkyllithium and -magnesium derivatives would be important reagents for preparing polyfluoroalkyl derivatives of other metals. So far this has not proved to be the case. Soon after the discovery of the perfluoroalkyl iodides, reactions between these compounds and alkali metals were investigated (1-4). Only with lithium was any success achieved, and even with this element perfluoroalkyl derivatives were at best difficult to form and, moreover, once produced readily decomposed or underwent reaction with the solvent. Thus, although trifluoromethyl iodide reacted slowly at room temperature and rapidly at 70°C with lithium in benzene, the only products were lithium fluoride and lithium iodide (6).

A more successful approach to the synthesis of perfluoroalkyllithium

compounds involved the use of exchange reactions. Perfluoro-*n*-propyl-lithium can be obtained in over 70% yield by the reaction (7),



Interestingly, on warming the mixture obtained by this interconversion to reflux temperature, hexafluoropropene was released in nearly quantitative yield. It is possible that decomposition of the perfluoro-*n*-propyllithium occurs via the reaction sequence

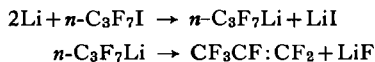


involving a fluorocarbanion (3). However, a different proposed mode of decomposition is described below.

At low temperatures perfluoro-*n*-propyllithium, prepared in the above manner, underwent displacement and addition reactions common to alkyl-lithium compounds. The experimental technique (7) involved adding methyllithium and the reactant dissolved in ether to heptafluoro-*n*-propyl iodide in the same solvent. In this manner, certain aldehydes and ketones afforded the expected alcohols, and diethyldichlorosilane gave a mixture of the organosilanes *n*-C₃F₇(C₂H₅)₂SiCl and (*n*-C₃F₇)₂Si(C₂H₅)₂.

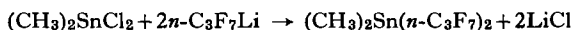
Attempts to obtain perfluoromethyllithium by treating trifluoromethyl iodide with methyllithium at low temperatures failed, even though a vigorous reaction was observed (7). Other workers (3), however, have claimed formation of CF₃Li in 20% yield by this exchange reaction.

Recently the direct synthesis and the stability of perfluoro-*n*-propyllithium has been the subject of a careful study (8). Although heptafluoro-propyl iodide does not react with lithium metal in pentane or diethyl ether at temperatures between -50° and 20° C, a vigorous reaction occurs at -74° C between the iodide and lithium containing 2% sodium when diethyl ether is the solvent. Among the reaction products are hexafluoropropene, fluorine-containing polymers, and a trace of heptafluoropropane. Formation of heptafluoropropane can be understood in terms of hydrogen abstraction from the solvent by perfluoro-*n*-propyllithium, while hexafluoropropene could form by the reactions,

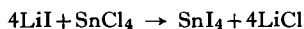
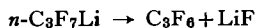
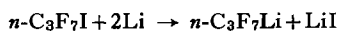


involving fluorine shift from the side chain to the metal, in a manner similar to the thermal decompositions of other fluorocarbon-metal com-

pounds mentioned later. Interestingly, heptafluoro-*n*-propyl iodide does not react with the lithium-sodium alloy in pentane. In tetrahydrofuran at -40°C the iodide and the alloy at first react exothermically, but reaction ceases when the alloy becomes coated with a brown deposit. Before this occurs heptafluoropropane and hexafluoropropene are formed in copious amounts, with the former predominating in the mixture. It is clear that perfluoro-*n*-propyllithium is produced readily in tetrahydrofuran but that hydrogen abstraction from this solvent is facile. Somewhat similar results are obtained when di(2-ethoxyethyl) ether is used as solvent. It can be said that with increasing solvation the instability of perfluoro-*n*-propyllithium with respect to forming $\text{CF}_3\text{CF}:\text{CF}_2$ and lithium fluoride decreases with the solvents examined, in the order: diethyl ether, tetrahydrofuran, di(2-ethoxyethyl) ether. Since, however, heptafluoropropane formation markedly increases in the same order, perfluoro-*n*-propyllithium is best formed in diethyl ether. By forming the perfluoroalkyllithium compound in the presence of dimethyldichlorosilane a 35% yield of the compound $(\text{CH}_3)_2\text{Si}(\text{C}_3\text{F}_7)_2$ was obtained (9). Similarly, addition of dimethyltin dichloride to heptafluoro-*n*-propyl iodide and lithium-sodium alloy afforded dimethylbis(perfluoropropyl)tin in good yield.

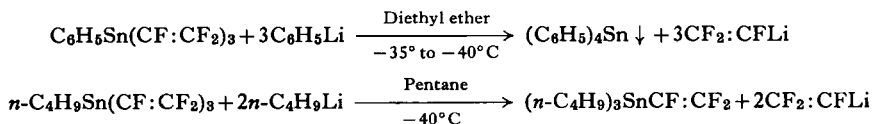


In an attempt to prepare $(\text{C}_3\text{F}_7)_4\text{Si}$, silicon tetrachloride was treated with the lithium alloy and heptafluoro-*n*-propyl iodide. Hexafluoropropene and a mixture of fluorosilanes, $(\text{C}_3\text{F}_7)_x\text{SiF}_{4-x}$, were formed. A similar reaction with tin tetrachloride led to formation of tin tetraiodide, very probably by the reaction sequence,

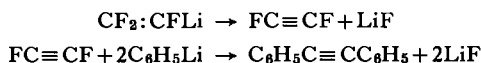


Indeed separate experiments showed that lithium iodide reacts both with tin tetrachloride and with germanium tetrachloride, so that perfluoro-*n*-propyllithium made via the lithium-sodium alloy cannot be used to prepare $(n\text{-C}_3\text{F}_7)_4\text{Sn}$ and $(n\text{-C}_3\text{F}_7)_4\text{Ge}$. Nevertheless, it is now established that perfluoro-*n*-propyllithium may be used to synthesize a number of new perfluoropropyl derivatives of Group IV elements, and probably similar compounds of other elements as well (9). As a result it is likely that perfluoroalkyllithium compounds will play a more important part in synthetic work in the future than they have in the past.

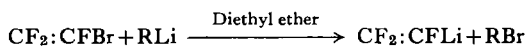
During the last few years extensive studies have been made on vinyl metallic compounds (10, 11), including the isolation of substances in which a $\text{CF}_2\text{:CF}$ group is linked to a metal (12–15). Consequently, perfluorovinyl lithium was prepared by the transmetallation reactions (15, 16):



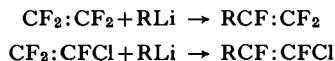
It will be noted that in the latter reaction removal of perfluorovinyl groups from tin is not complete. The perfluorovinyl lithium reagent, a reddish brown solution in diethyl ether, was well characterized by using it to prepare the compounds $(\text{C}_2\text{H}_5)_3\text{SnCF}_2\text{:CF}$, $(\text{CH}_3)_3\text{SnCF}_2\text{:CF}$, and $(\text{CH}_3)_3\text{SiCF}_2\text{:CF}$ from the appropriate halides, and by addition of carbon dioxide to produce $\text{CF}_2\text{:CFCOOH}$. The stability of perfluorovinyl lithium is markedly affected by concentration and temperature. It completely decomposes above 0°C , and it is important to add the phenyllithium slowly, using dilute solutions of the reactants. Concentrated solutions ($\sim 30\%$) of perfluorovinyl lithium decompose rapidly and sometimes explode, suggesting that difluoroacetylene is an intermediate. In this connection it is interesting that treatment of perfluorovinyl lithium with a ninefold excess of phenyllithium affords diphenylacetylene, probably via the reaction sequence,



Searching for a more satisfactory and direct way to prepare perfluorovinyl lithium, Tarrant and co-workers (17) found that bromotrifluoroethylene would react with alkyl lithium compounds with metal-halogen exchange.

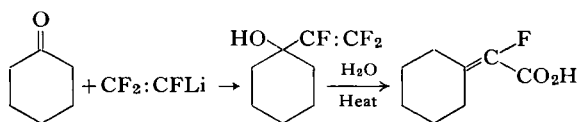


This discovery is novel in view of the earlier observation (18) that tetrafluoroethylene and chlorotrifluoroethylene react with alkyl lithium compounds in a different manner,



In preparing perfluorovinyl lithium from bromotrifluoroethylene both methyl- and *n*-butyllithium have been used, affording the desired lithium compound in approximately 70% yield. A study (17) was made of the thermal

stability of the lithium reagent in diethyl ether at 0° , -27° , and -78°C . The extent of decomposition was determined from the yield of acid recovered from the reaction,

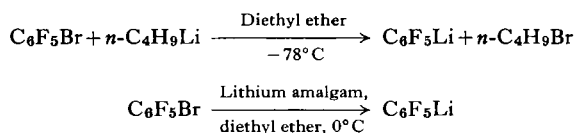


It was found that in diethyl ether at -78°C perfluorovinyl lithium is stable for approximately 1 hour, but after 24 hours some 37% of the reagent had decomposed. Addition of portions of cyclohexanone 30 seconds after each aliquot of methyl lithium had been added to bromotrifluoroethylene gave yields of the acid of 69%, 56%, and 50% at -78° , -27° , and 0°C , respectively. As in the synthesis of perfluorovinyl lithium by transmetallation, the observation was made that concentration is an important factor in the stability of the reagent. Thus when the entire amount of methyl lithium was added to bromotrifluoroethylene at -27°C and the cyclohexanone added 2 minutes later, no cyclohexylidenefluoroacetic acid was obtained after the subsequent work-up.

An examination was made of the nature of the decomposition products of perfluorovinyl lithium. Bromotrifluoroethylene was treated with butyllithium at -78°C using a mixture of pentane and hexane as solvent. The solution was warmed slowly to room temperature and lithium fluoride, butyl bromide, and fluorine-containing polymer were produced. Interestingly, the polymer was relatively rich in hydrogen, suggesting incorporation of the solvent in the decomposition process. From this study and that mentioned previously (16) it would appear that the mode of decomposition of perfluorovinyl lithium is complicated and has not yet been elucidated.

It is probable that perfluorovinyl lithium will be used extensively for synthetic work in the field of fluorocarbon-metal compounds. It has the advantage that it can be used in hydrocarbon solvents, unlike perfluorovinylmagnesium bromide (Section III) which is prepared in tetrahydrofuran.

Current interest in aromatic fluorine chemistry has led to the preparation of pentafluorophenyl lithium (19).



If the halogen-alkyl metal exchange is carried out above -20°C , fluoride ion is formed, together with intractable organic material. Similarly, above 0°C the metallation reaction led to fluoride ion formation.

Pentafluorophenyllithium was characterized by treating it with water to give pentafluorobenzene, with ethyl formate or *N*-methylformanilide to give pentafluorobenzaldehyde, and with benzaldehyde to give α -pentafluorophenylbenzyl alcohol.

Pentafluorophenyllithium was shown (19) to be more stable than *o*-fluoro- and *o*-bromophenylmagnesium halides. At 0°C pentafluorophenyllithium was formed in 77% yield,⁴ and after 24 hours at -10°C , 58% of the reagent was still present. In displaying relatively high stability the lithium compound is similar to pentafluorophenylmagnesium bromide. It has been suggested that the enhanced stabilities of $\text{C}_6\text{F}_5\text{Li}$ and $\text{C}_6\text{F}_5\text{MgBr}$ are a consequence of the stabilization of the carbanion by five electron-withdrawing fluorine atoms.

Pentafluorophenyllithium in ether reacts slowly with mercury at 15°C to afford bis(pentafluorophenyl)mercury, a compound recently prepared by another route (Section VII, B). The lithium reagent has very recently been used to prepare pentafluorophenyl derivatives of boron (19a), tin (19b), lead (19b), and several transition metals (19c).

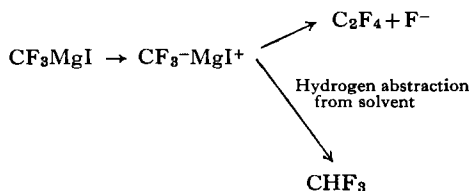
III

MAGNESIUM DERIVATIVES

The difficulty of forming Grignard reagents from perfluoroalkyl iodides is exemplified by early work involving trifluoromethyl and pentafluoroethyl iodides (6). After treating a sample of trifluoromethyl iodide with magnesium in diethyl ether at room temperature for six weeks 91% of the iodide was recovered. Typical catalysts used to initiate Grignard formation had no effect. On the other hand, with pentafluoroethyl iodide a different problem was encountered. Reaction with magnesium in diethyl ether took place with complete decomposition, and production of carbonaceous residue. Subsequently, formation of perfluoromethylmagnesium iodide was claimed (20). It was found that preparation of this Grignard reagent was dependent on the purity of the magnesium used, on the temperature, on the basicity of the ether, and on the concentration of the perfluoroalkyl iodide. Exceedingly

⁴ Determined by titration of the ethereal solution with aqueous acid.

pure magnesium and low temperatures (-20° to -40°C) are essential for formation of perfluoromethylmagnesium iodide, and even if these conditions are met reproducible results are not always obtained. It is suggested(20) that the reagent decomposes by two routes:



Much less difficulty has been encountered in forming perfluoro-*n*-propylmagnesium iodide, reported by three groups of workers (21-23). This Grignard reagent is reasonably stable at low temperatures but decomposes rapidly at ambient temperatures. It is convenient, therefore, to initiate Grignard formation at about 20°C and then to cool the reaction vessel before addition of the remaining heptafluoro-*n*-propyl iodide. In this way Henne and Francis (21) obtained $\text{C}_3\text{F}_7\text{COOH}$ in 45% yield by producing the Grignard reagent in the presence of solid carbon dioxide at -80°C . At room temperature or above, perfluoro-*n*-propylmagnesium iodide forms perfluoropropene and fluoride ion, and if diethyl ether is used as solvent attack on the latter affords C_2H_6 , $\text{C}_3\text{F}_7\text{H}$, and $\text{C}_3\text{F}_7\text{CH}(\text{OH})\text{CH}_3$ (23). In preparing perfluoro-*n*-propylmagnesium iodide, the more basic the solvent the better the yield, and in this connection it is interesting to note that tetrahydrofuran was used as a solvent in which to form the reagent (22) some years before it was generally recognized that this ether is especially useful as a medium for reactions between magnesium and inert halides, e.g. vinyl halides (24, 25).

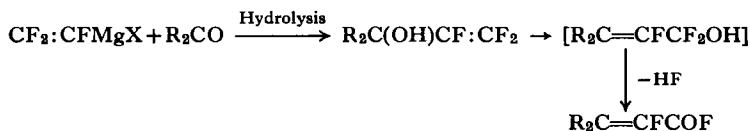
Perfluoro-*n*-propylmagnesium iodide has been treated with a number of compounds possessing carbonyl groups, thereby producing a variety of organic compounds containing *n*- C_3F_7 groups (26). Even allowing for its low thermal stability the ready formation of perfluoro-*n*-propylmagnesium iodide suggests that it could be used to prepare a number of as yet unknown perfluoro-*n*-propyl metal compounds.

It is perhaps worthwhile mentioning that the perfluoro-*n*-propyl Grignard reagent has also been made by treating phenylmagnesium bromide with heptafluoro-*n*-propyl iodide, thereby causing an exchange reaction to occur (27, 28). This route to the Grignard is probably now only of academic interest.

It was mentioned earlier that pentafluoroethyl iodide was decomposed by magnesium in ether. Nevertheless, it has been possible to prepare several perfluoroethyltin compounds (Section V, C) by adding pentafluoroethyl iodide to a mixture of alkyltin chlorides and magnesium in tetrahydrofuran at room temperature (29). Yields of the desired product can be as high as 50%.

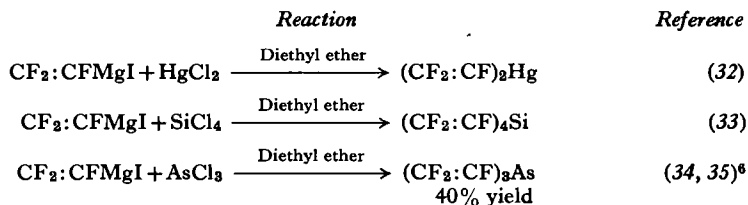
Much less difficulty has been encountered in preparing Grignard reagents containing $\text{CF}_2\text{:CF}$ and C_6F_5 groups than those containing perfluoroalkyl groups. Park and co-workers (12) found that iodotrifluoroethylene will react with magnesium in diethyl ether to form perfluorovinylmagnesium iodide. Subsequently, perfluorovinylmagnesium iodide was obtained by other workers (13) who noted that yields were improved if the reaction was carried out at low temperatures. Thus, formation of the Grignard at -20°C followed by hydrolysis can give trifluoroethylene in about 70% yield.

Iodotrifluoroethylene is relatively inaccessible. Fortunately, therefore, two groups of workers (13, 14) independently found that the more readily obtainable bromotrifluoroethylene⁵ will form a Grignard reagent in reasonable yield in tetrahydrofuran at low temperatures. Reactions between the perfluorovinyl Grignard reagent and a number of organic compounds have been studied and some novel results obtained (30, 31). Simple aldehydes and ketones afford α -fluoro- α , β -unsaturated acid fluorides.



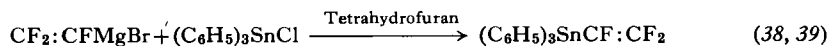
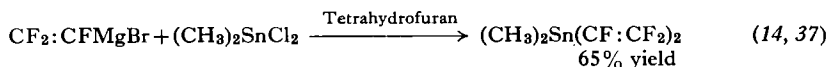
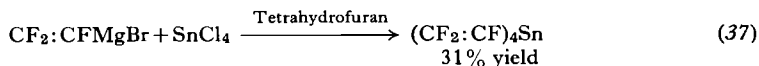
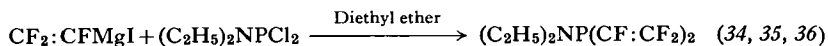
Trifluoroacetaldehyde and trifluoroacetone, on the other hand, afford predominantly the expected alcohol rather than the rearranged acid fluoride.

The perfluorovinyl Grignard reagent has been very useful in preparing perfluorovinyl compounds of many elements. For example,



⁵ Commercially available in the United States (Columbia Chemical Co. and Peninsular Chemical Co.).

⁶ See also ref. (14) for preparation of tris(perfluorovinyl)arsine from bromotrifluoroethylene.



In reactions involving bromotrifluoroethylene, increased yields of the desired product can be obtained by addition of the halide to a mixture of magnesium, the substance to be perfluorovinylated, and tetrahydrofuran (37). Equally satisfactorily a mixture of bromotrifluoroethylene and the metal halide in tetrahydrofuran may be added to magnesium in tetrahydrofuran (39).

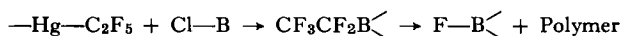
Both pentafluorophenylmagnesium iodide and bromide have been reported (40–43). Apparently these reagents are readily formed from the appropriate halide and magnesium in diethyl ether. Pentafluorophenylmagnesium bromide has been used to prepare $(\text{C}_6\text{F}_5)_4\text{Si}$ (32% yield) and $(\text{C}_6\text{F}_5)_3\text{P}$ (39.5% yield), as well as several pentafluorophenyltin compounds (Section V, C).

IV

DERIVATIVES OF GROUP IIIb ELEMENTS

A. Boron

Several attempts were made to prepare compounds having a perfluoroalkyl group bonded to boron before success was achieved. In the case of tricoordinate boron compounds, $\text{R}_\text{F}-\text{B}$ linkages were expected to be unstable because of the inability of R_F groups to relieve the electrophilic character of the boron atom by π bonding (44). In confirmation of this idea, bis(perfluoroalkyl)mercury compounds [e.g., $(\text{C}_2\text{F}_5)_2\text{Hg}$] afford boron trifluoride when heated with boron trichloride (45, 46). Boron trifluoride formation presumably occurs via a transitory $\text{R}_\text{F}-\text{B}$ derivative:



Migration of a fluorine atom in the organic side chain to boron is related to the decomposition of perfluoroalkyllithium and fluorocarbon Grignard

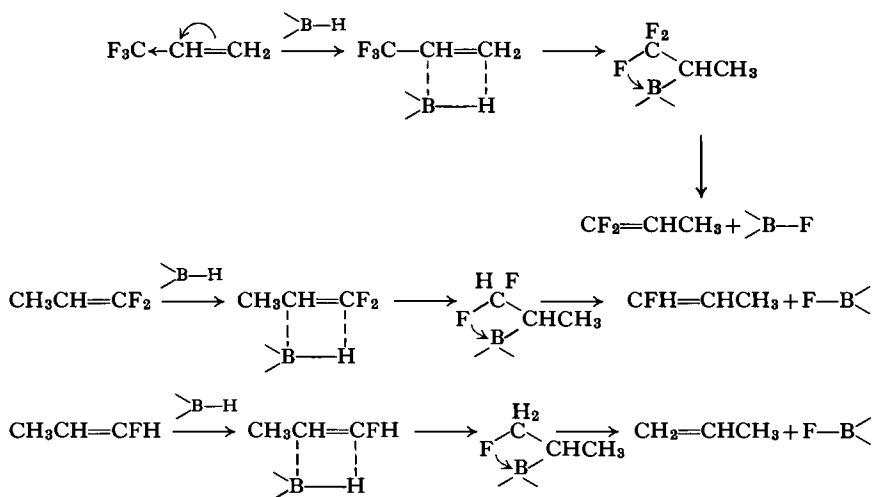
reagents discussed above, and to the decomposition of $(\text{CH}_3)_3\text{SnCF}_3$ and perfluoroalkyl transition metal compounds discussed in later sections of this chapter. It is generally observed that when a fluorocarbon group is bonded to a metal having a vacant or potentially vacant orbital, transfer of fluorine from the side chain to the metal can occur under suitable conditions. This mechanistically favorable route for decomposition, very probably involving little activation energy, is aided by the relatively high thermodynamic stability of metal-fluorine bonds. In spite of this problem several fluoro-carbon derivatives of boron have been described.

Goubeau and Rohwedder (47) found that gaseous boron trifluoride and diazomethane reacted to form the fluoroalkylboron compound FCH_2BF_2 , a liquid between -47° and 7°C . This substance has several properties which suggest interaction between the fluorine atom of the side chain and the boron atoms of the same molecule, or the boron atoms of other molecules. Thus FCH_2BF_2 decomposes to give boron trifluoride, while its vapor density and high Trouton constant suggest association, viz.,

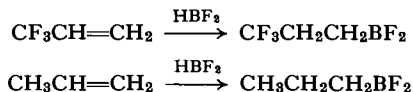


Metastable CF_3BF_2 has been claimed as a product of two different reactions (48). Addition of trifluoromethyl iodide to a diethyl ether solution of $(n\text{-C}_4\text{H}_9)_2\text{BK}$ afforded potassium iodide and a pale yellow solution presumably containing $(n\text{-C}_4\text{H}_9)_2\text{BCF}_3$ -etherate or some more complex system having $\text{B}-\text{CF}_3$ bonds. The filtered solution reacted with boron trifluoride to give *n*-butylboron difluoride and the presumed CF_3BF_2 . Decomposition of the latter into boron trifluoride and $(\text{CF}_2)_n$ was found to be catalyzed by oxygen and by glyptal. Alternatively, treatment of CF_3SCl with diborane at 60°C afforded a complex mixture of H_2 , BF_3 , B_2H_6 , CF_3SH , and CF_3SSCF_3 , as well as CF_3BF_2 . Hydrogen, boron trifluoride, and diborane were easily removed by distillation in the vacuum system but in order to recover CF_3BF_2 from the sulfur compounds dimethyl ether was added so as to form the etherate, $(\text{CH}_3)_2\text{O}\cdot\text{BF}_2\text{CF}_3$. Addition of boron trifluoride to the etherate did not release CF_3BF_2 . This is not unexpected since CF_3BF_2 should be a stronger Lewis acid than boron trifluoride. Unfortunately no further information is at present available about the properties of CF_3BF_2 . Evidently the compound has been obtained in only very small quantity, and its chemistry and physical properties have not been fully investigated. For example, no mention has been made of its rate of decomposition into boron trifluoride.

Related to the decomposition of the compounds FCH_2BF_2 and CF_3BF_2 is the nature of the products obtained from reactions between diborane and the fluoroethylenes or 3,3,3-trifluoropropene, as well as the decomposition of dimethyl-1-(trifluoromethyl)ethylboron. Whereas diborane and olefins react to form trialkylboron compounds, tetrafluoroethylene, trifluoroethylene, 1,1-difluoroethylene, and vinyl fluoride all react to yield boron trifluoride, ethylboron difluoride, and diethylboron fluoride as the principal products (49). Similarly, diborane and 3,3,3-trifluoropropene afford many products including 1,1-difluoropropene, 1-fluoropropene, boron trifluoride, *n*-propylboron difluoride, and 3,3,3-trifluoropropylboron difluoride (50). As with the reactions between diborane and the fluoroethylenes, the nature of these products can be understood in terms of fluorine shifts, as well as addition of B—H linkages to unsaturated molecules. These processes would involve many different molecular species and transformations (49, 50). For example,

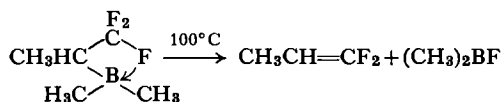


and



The thermal stability of 3,3,3-trifluoro-*n*-propylboron difluoride is relatively high, the compound being only about 8% decomposed after heating for several days at 160°C. Moreover, 1,1-difluoropropene is not an observed

decomposition product. Apparently when the fluorine atoms associated with an organic side chain bonded to boron are in the γ position, fluorine shift to boron does not occur. In contrast the reaction,



involving β fluorine shift, has been observed (51).

These results show clearly that if stable organoboron compounds having fluorine in the α or β positions to boron are to be obtained, the electrophilic nature of the boron atom must be reduced; otherwise formation of a boron fluoride will occur. Recognition of this principle, involving reduction of the acceptor power of the boron atom, has resulted in considerable progress in isolating compounds having fluorocarbon groups linked to boron. One method of reducing the Lewis acidity of a tricoordinate boron atom is to link to boron groups able to π -bond strongly with the boron p orbital. Alternatively, if boron is made tetracoordinate its acceptor properties will be removed entirely, since all stable orbitals will be used in bonding. Both of these approaches to the problem have been used successfully.

There is a considerable body of evidence for believing that in vinylboron compounds like $\text{CH}_2:\text{CHBF}_2$ there is interaction between the vinyl group's π electrons and the adjacent boron p_π orbital, thereby reducing Lewis acidity (52, 53). In view of this it seemed likely that tricoordinate perfluorovinylboron compounds would exist, and it was found possible to obtain these substances via perfluorovinyltin compounds (54). Dimethylbis(perfluorovinyl)tin reacts with boron trichloride below 100°C to form either perfluorovinylboron dichloride or bis(perfluorovinyl)boron chloride as the principal product, depending on the ratio of the reactants. Perfluorovinylboron difluoride can be obtained by fluorination of perfluorovinylboron dichloride with antimony trifluoride below 0°C , while tris(perfluorovinyl)boron is satisfactorily prepared from bis(perfluorovinyl)boron chloride and dimethylbis(perfluorovinyl)tin. Physical properties of the perfluorovinylboron compounds are listed in Table I. Until the recent discovery (19a) of tris(pentafluorophenyl)boron, described below, these substances were the only covalent organoboron compounds reported which contain no hydrogen atoms in the group bonded to boron, although a boron-substituted perfluoro- n -propylborazole had been briefly mentioned, but no properties of this compound have been given (45).

The perfluorovinylboron compounds are remarkably thermo-stable, in view of the easy decomposition, discussed above, of their polyfluoroalkyl analogs. Perfluorovinylboron dichloride can be heated briefly to 100°C without decomposition, but on standing for a few days at room temperature it partially decomposes, giving boron trifluoride. Similar observations have been made on the other perfluorovinylboron compounds. These substances burn in air, and may even detonate in the presence of oxygen. They are hydrolyzed by water at elevated temperature, releasing trifluoroethylene.

TABLE I
PHYSICAL PROPERTIES OF SOME PERFLUOROVINYLBORON COMPOUNDS

Compound	M.p. ^a (°C)	Log <i>p</i> (mm) = <i>B</i> - <i>AT</i> ⁻¹		B.p. ^b (°C)	Trouton const. ^b (eu)	ΔH_{vap} (kcal/ mole)
		<i>B</i>	<i>A</i>			
CF ₂ :CFBF ₂	- 96	8.247	1389	-14.0	24.6	6.39
CF ₂ :CFBCl ₂	-108	8.008	1645	48.0	23.4	7.53
(CF ₂ :CF) ₂ BCl	- 57.5	7.861	1861	100.5	22.8	8.52
(CF ₂ :CF) ₃ B	-107	8.559	2147	104.9	26.0	9.83

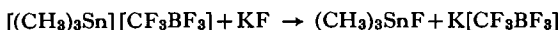
^a Stock magnetic plunger method.

^b By extrapolation of the vapor pressure equation.

Cleavage of the organo-group in this way is more facile than the corresponding reaction involving ordinary vinylboron compounds. As described in Section V, C, vinyl- and perfluorovinyltin compounds differ in the same way. The existence of the perfluorovinylboron compounds can be reasonably understood in terms of a mesomeric effect involving the π electrons of the perfluorovinyl group and the adjacent boron p_{π} orbital. In this way the CF₂:CF—B group is stabilized, although not completely so, as evidenced by the boron trifluoride formation mentioned above. The concept of carbon-boron π bonding in the perfluorovinylboron compounds is supported by infrared and F¹⁹ NMR studies (53, 55, 56).

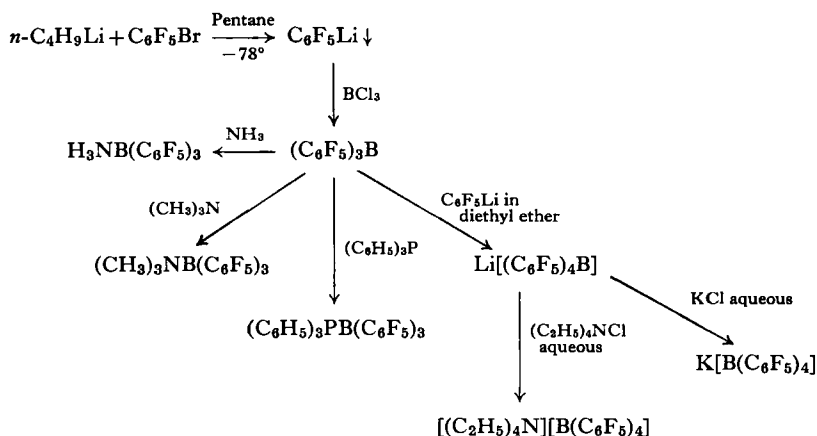
Clark and co-workers (57) have isolated several salts containing the anion [CF₃BF₃]⁻. Treatment of trimethylperfluoromethyltin with boron trifluoride in carbon tetrachloride afforded ionic [(CH₃)₃Sn] [CF₃BF₃] as a hygroscopic white solid. The latter is precipitated on warming the reactants

from -196° to 20° C. On standing $[(\text{CH}_3)_3\text{Sn}][\text{CF}_3\text{BF}_3]$ slowly evolves boron trifluoride. It is soluble in water, affording a stable solution. On addition of potassium fluoride the reaction,



occurs. Barium and ammonium salts of the anion $[\text{CF}_3\text{BF}_3]^-$ can be obtained using an ion exchange resin column. The salt $\text{K}[\text{CF}_3\text{BF}_3]$, freely water soluble in contrast to potassium borofluoride, is stable *in vacuo* below 300° C. Above this temperature tetrafluoroethylene, perfluorocyclobutane, perfluorocyclopropane, and potassium borofluoride are produced. The stability of the anion $[\text{CF}_3\text{BF}_3]^-$ is undoubtedly due to the fact that all stable boron orbitals are employed in σ bond formation, so that fluorine shift to a vacant orbital is not possible. A further factor favoring stability, however, might be distribution of the negative charge over all six fluorine atoms in the anion (57).

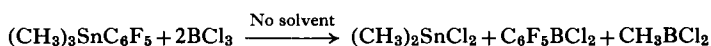
Preparation of pentafluorophenyllithium in ether was mentioned in Section II. It has recently been found possible to precipitate this reagent as a white solid from pentane by adding pentafluorophenyl bromide to butyllithium dissolved in the hydrocarbon (19a). Formation of the lithium reagent from pentane, rather than as a solution in diethyl ether, has proved advantageous in the preparation of several pentafluorophenylboron compounds, according to the following scheme:



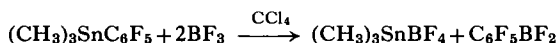
Tris(Pentafluorophenyl)boron can be obtained as a white, very air-sensitive, solid (m.p. $132\text{--}134^{\circ}$) by evaporation of its pentane solution (19a). If ether is used as the reaction medium pentafluorophenylboron etherates are pro-

duced. Pentafluorophenylboron compounds are apparently strong Lewis acids since once etherates are formed further chemical transformations are difficult.

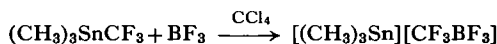
There has been a preliminary report (57a) of the synthesis of pentafluorophenylboron halides by cleavage of pentafluorophenyl groups from pentafluorophenyltin compounds by boron halides. This synthesis is analogous to that used to obtain perfluorovinylboron compounds, described above.



However, the reaction



is in contrast to



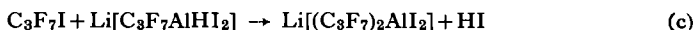
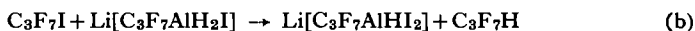
referred to above. It would thus appear that pentafluorophenylboron difluoride is a weaker acid than boron trifluoride which in turn is a weaker acid than perfluoromethylboron difluoride.

It seems reasonable to suggest that tris(pentafluorophenyl)boron and the pentafluorophenylboron halides owe their existence to C—B π bonding.

B. Aluminum

Relatively little is as yet known about fluorocarbon derivatives of aluminum. As in the case of boron, the compounds are likely to be inherently unstable unless formation of Al—F bonds can be hindered.

Heptafluoro-*n*-propyl iodide reacts with lithium aluminum hydride according to the equations (58):



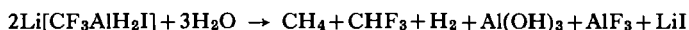
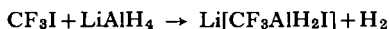
If heptafluoropropyl iodide is added to an ethereal solution of lithium aluminum hydride under dilute conditions at low temperatures a vigorous evolution of hydrogen gas occurs. This gas evolution ceases after one mole of the iodide has been added to one mole of the hydride [reaction (a)]. Addition of water at this stage leads to a reaction which may be represented by the equation,



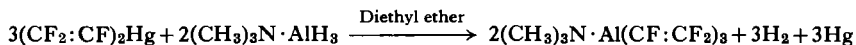
After one mole of heptafluoropropyl iodide has been added to one mole of lithium aluminum hydride, further addition of the iodide leads to formation of heptafluoropropane but no additional hydrogen [reaction (b)]. A third mole of heptafluoropropyl iodide reacts more slowly, in accordance with reaction (c). Only after addition of 3 moles of heptafluoropropyl iodide to the original one mole of lithium aluminum hydride did the resulting ethereal solution fail to liberate hydrogen upon addition of water.

The stability of $\text{Li}[\text{C}_3\text{F}_7\text{AlH}_2\text{I}]$ in ether was studied (58) by refluxing the solution at 35–40° C for a few hours. On addition of water only 41% of the expected quantity of hydrogen gas and 54% of the expected quantity of heptafluoropropane were obtained. An attempt to isolate $\text{Li}[\text{C}_3\text{F}_7\text{AlH}_2\text{I}]$ by evaporation of the ether solution led to vigorous decomposition. Perhaps anions like $[\text{C}_3\text{F}_7\text{AlH}_2\text{I}]^-$ are stabilized in ether by coordination of the solvent to the aluminum so that maximum possible use is made of the metal's orbitals in bonding. Such stabilization would be similar to that believed to be chiefly responsible for the existence of $[\text{CF}_3\text{BF}_3]^-$, mentioned in the preceding section.

Reaction between approximately equimolar quantities of trifluoromethyl iodide and lithium aluminum hydride in diethyl ether at –78° C, followed by addition of water, has been represented (58) by the equations,



Tris(perfluorovinyl)aluminum has been obtained as its trimethylamine adduct by the novel reaction (59),



The reactants are mixed at –20° C, and the mixture subsequently stirred at room temperature with addition of further bis(perfluorovinyl)mercury. This is necessary to effect conversion of the intermediate $(\text{CH}_3)_3\text{N} \cdot \text{Al}(\text{CF}:\text{CF}_2)_2\text{H}$ into $(\text{CH}_3)_3\text{N} \cdot \text{Al}(\text{CF}:\text{CF}_2)_3$. Trimethylamine–tris(perfluorovinyl)aluminum is a colorless air-sensitive liquid which may be distilled under high vacuum (42.5° C/10^{–3} mm). It may be stored for weeks at –20° C, but at room temperature it darkens and become viscous. Treatment with water affords trifluoroethylene. Molecular weight studies in cyclohexane indicate that the perfluorovinylaluminum compound is highly associated.

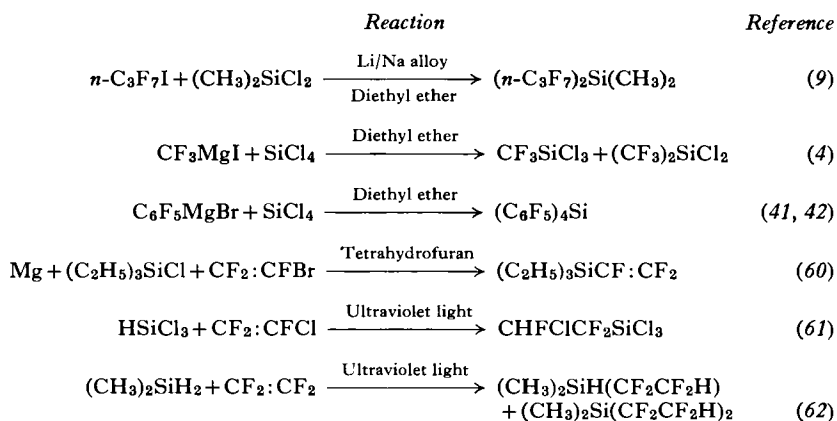
V

DERIVATIVES OF GROUP IVb ELEMENTS

A. Silicon

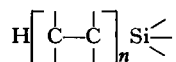
Many organosilanes are known in which fluorocarbon groups are bonded to silicon. These compounds are of many types, for example: $\text{H}(\text{CF}_2)_4\text{SiCl}_3$, $(\text{CF}_3)_2\text{SiCl}_2$, $(\text{CF}_2:\text{CF})_4\text{Si}$, *trans*-(C_2H_5)₃SiCF:CFCH:CH₂, and $(\text{C}_6\text{F}_5)_4\text{Si}$. A recent review (5) has provided a comprehensive survey of polyfluoroalkyl- and perfluoroalkylsilicon compounds.⁷ For this reason detailed discussion of these substances will not be given here; only general properties and new reactions will be described. It is worth recording that initial interest in polyfluoroalkylsilicon compounds arose from the possibility that a silicone polymer having fluorocarbon groups attached to silicon might have superior thermal and other properties compared with those of conventional silicones. However, as described below, polyfluoroalkylsilicon groups having fluorine atoms in α - or β -positions to silicon are decomposed by aqueous base, and tend to form Si—F linkages on heating. Only if the fluorine is present in the polymer in such groups as $[\text{CF}_3\text{CH}_2\text{CH}_2\text{—SiO}_{1.5}]_n$ are improved properties sometimes observed.

There are several different methods by which fluorocarbon groups can be linked to silicon. Some of these syntheses have been mentioned in previous sections. For convenience, the preparative routes employed are summarized here.

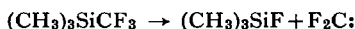


⁷ Table IV in ref. (5) provides a valuable list of physical properties.

The reactions involving addition of Si—H linkages to chlorotrifluoroethylene or tetrafluoroethylene should be compared with reactions used to prepare $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CF}_2\text{CF}_2\text{H})_2$ (Section V, C), and $(\text{CO})_5\text{MnCF}_2\text{CFCIH}$ and $(\text{CO})_5\text{MnCFCICF}_2\text{H}$ (Section VI, B). Addition of Si—H groups to fluoroolefins yields products of the type



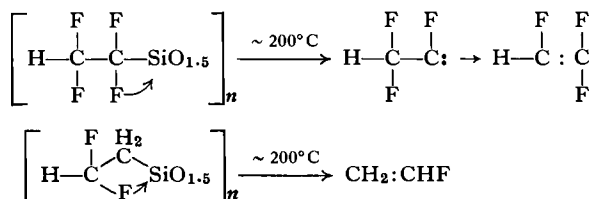
as well as those mentioned above. The value of n depends on the ratios of the reactants and the olefin used. A valuable reaction for preparing organosilicon halides involves passing organic halides over silicon in the presence of copper (63, 64). Patent claims⁸ have been made that the direct reaction may also be used to prepare perfluoroalkylsilicon halides, for example, $(\text{C}_2\text{F}_5)_2\text{SiCl}_2$ from $\text{C}_2\text{F}_5\text{Cl}$ and silicon-copper mixture. From what is now known about the properties of perfluoroalkyl compounds of Group IV elements this method of synthesis seems improbable, except to form trace amounts of fluorides such as CF_3SiF_3 . In the same category are unsuccessful attempts made to form compounds $\text{R}_3\text{SiR}_\text{F}$ by cleavage of silicon-silicon bonds in disilanes, R_3SiSiR_3 , with perfluoroalkyl iodides. The dissociation energy of the silicon-silicon bond is high (81 kcal), in fact comparable with that (83 kcal) of the carbon-carbon bond (65). Hence under those conditions where perfluoroalkyl iodides react with disilanes, the $\text{R}_3\text{SiR}_\text{F}$ compounds formed would be expected to decompose rapidly, e.g.,



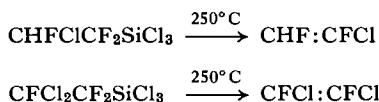
Hydrolysis of polyfluoroalkylsilicon di- or trihalides with water affords polyfluoroalkylsilicon polymers (66). However, even dilute aqueous alkali cleaves the silicon-carbon bonds of these polymers at room temperature when fluorine is in either the α - or the β -positions. Fluorocarbon groups in nonpolymeric compounds like $\text{CHF}_2\text{CF}_2\text{SiCl}_3$ or $(\text{CH}_3)_2\text{Si}(\text{C}_3\text{F}_7)_2$ are also easily removed as fluoroalkanes with aqueous base. Nucleophilic attack on silicon is evidently favored by the electronegative polyfluoroalkyl groups. When fluorine is not in the α - or β -positions, as in $(\text{CF}_3\text{CH}_2\text{CH}_2\text{SiO}_{1.5})_n$, strong aqueous alkali fails to cleave silicon-carbon bonds even at elevated temperatures.

⁸ See ref. (5), and references cited therein.

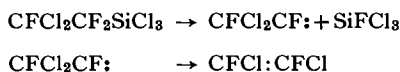
Pyrolysis of polyfluoroalkylpolysiloxanes leads to transfer of fluorine (66).



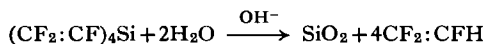
When fluorine is in both the α - and the β -positions, thermal degradation takes place by both α - and β -fluorine shift. Support for the mechanism involving a carbene is provided by pyrolysis studies on the compounds $\text{CHFClCF}_2\text{SiCl}_3$ and $\text{CFCl}_2\text{CF}_2\text{SiCl}_3$ (67):



These decompositions gave only small amounts of those olefins ($\text{CF}_2:\text{CHCl}$ and $\text{CF}_2:\text{CCl}_2$) which would form by release of fluorine from the β -position with respect to silicon. It seems reasonable to suppose that the initial step in pyrolysis involves internal nucleophilic attack on silicon by a fluorine in the α -position, followed by migration of an atom other than fluorine from the β -carbon atom.

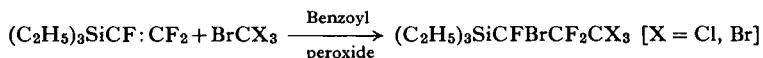


Discovery of the perfluorovinyl Grignard reagent resulted in the preparation of the perfluorovinylsilicon compounds: $(\text{CF}_2:\text{CF})_4\text{Si}$ (33); $(\text{C}_2\text{H}_5)_2\text{Si}(\text{CF}:\text{CF}_2)_2$ (55); $(\text{C}_2\text{H}_5\text{O})_3\text{SiCF}:\text{CF}_2$ and $(\text{C}_2\text{H}_5)_3\text{Si}(\text{CF}:\text{CF}_2)$ (60). The $\text{CF}_2:\text{CF}-\text{Si}$ group is stable to aqueous acids (compare $\text{CF}_2:\text{CF}-\text{Sn}$ discussed below) but aqueous potassium hydroxide displaces the perfluorovinyl groups (33).



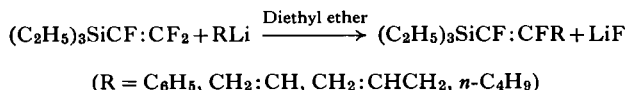
Several addition reactions of triethylperfluorovinylsilane have been reported (68). Bromine adds to give $(\text{C}_2\text{H}_5)_3\text{SiCFBrCF}_2\text{Br}$, and hydrogen bromide at -20°C to give $(\text{C}_2\text{H}_5)_3\text{SiCFHCF}_2\text{Br}$. With chlorine in carbon tetrachloride at 0°C , however, chlorination of the ethyl groups of triethylperfluorovinylsilane occurs, rather than addition. Trifluoromethyl iodide

adds to the perfluorovinyl group to give an unstable compound presumed to be $(C_2H_5)_3SiCFICF_2CF_3$. The reactions,



were also observed. The structures of the fluoro groups in $(C_2H_5)_3SiCFBrCF_2CCl_3$ and $(C_2H_5)_3SiCFHCF_2Br$ were established by a study of their F^{19} NMR spectra (68). During the course of the work it was shown that addition of reagents to the $Si-CF:CF_2$ group was less facile than addition to the $Si-CH:CH_2$ group.

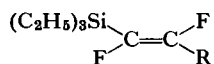
It has been mentioned previously (Section II) that perfluorovinyl lithium is formed by an exchange reaction when perfluorovinyltin compounds are treated with organolithium reagents. However, the latter are known to add to the double bonds of vinylsilicon compounds. In view of observations such as these it was important to determine the effect of organolithium compounds on a perfluorovinylsilane. This has been investigated using triethylperfluorovinylsilane (60). Exchange reactions do not occur; instead β -organo- α , β -difluorovinyltriethylsilanes are formed.



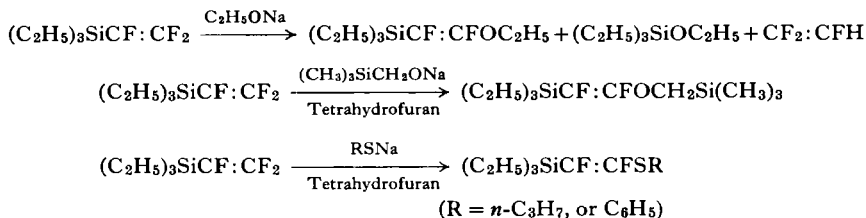
Organolithium reagents react with chlorotrifluoroethylene and tetrafluoroethylene in the same way (18, 69-71). The mechanism of these reactions is best interpreted in terms of addition followed by elimination of lithium fluoride (60).



Similar addition-elimination reactions were found with phenylmagnesium bromide, and with the lithium compounds $(C_6H_5)_3SiLi$, $(C_6H_5)_3GeLi$, and $(C_6H_5)_2PLi$. In this manner the compounds $(C_2H_5)_3SiCF:CFC_6H_5$, $(C_2H_5)_3SiCF:CFSi(C_6H_5)_3$, $(C_2H_5)_3SiCF:CFGe(C_6H_5)_3$, and $(C_2H_5)_3SiCF:CFP(C_6H_5)_2$ were obtained. The structures of these compounds were determined by F^{19} NMR spectroscopy. All the organic groups introduced by the lithium reagents are in the *trans*-position.



In addition to organolithium reagents, several other nucleophiles undergo addition-elimination reactions with triethylperfluorovinylsilane (60).

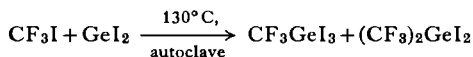


The compound from sodium thiophenolate was produced as an isomeric mixture of *trans* and *cis* forms.

B. Germanium

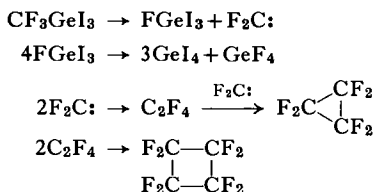
Until recently fluorocarbon derivatives of germanium were unknown. However, the isolation of perfluorovinyl and perfluoroalkyl compounds of silicon and tin suggested that a number of germanium analogs should exist. As yet few have been characterized but several synthetic routes are now obvious, such as the addition of germanium-hydrogen bonds to fluoroolefins, and treatment of germanium halides with appropriate Grignard and lithium reagents. Thus the compounds $(\text{CF}_2:\text{CF})_4\text{Ge}$ and $(\text{CH}_3)_2\text{Ge}(\text{CF}:\text{CF}_2)_2$ were prepared for spectroscopic studies (55, 56) from perfluorovinylmagnesium bromide and germanium tetrachloride and dimethylgermanium dichloride, respectively. Subsequently $(\text{C}_2\text{H}_5)_3\text{GeCF:CF}_2$ and $(\text{C}_6\text{H}_5)_3\text{GeCF:CF}_2$ were reported (60). Moreover, the observation (Section V, A) that organolithium reagents react with triethylperfluorovinylsilane to give the compounds *trans*-($\text{C}_2\text{H}_5)_3\text{SiCF:CFR}$, led to the synthesis of $(\text{C}_2\text{H}_5)_3\text{-SiCF:CFGe}(\text{C}_6\text{H}_5)_3$ (60).

A novel route for synthesizing perfluoromethylgermanium compounds has recently been described (72). It depends on the ability of germanium(II) halides to function as reducing agents so that the reaction

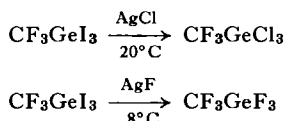


occurs. The principal product is trifluoromethyltriiodogermane, a dense light yellow liquid (m.p. 8.4°C ; vapor pressure at ambient temperatures, 0.2–0.5 mm). Attempts to prepare CF_3SnI_3 from stannous iodide by a similar reaction were unsuccessful.

At 180° C trifluoromethyltriiodogermane slowly decomposes, affording germanium tetrafluoride and tetraiodide, fluoroolefins, and cyclic fluorocarbons. The nature of these products suggests the occurrence of the reactions,



Trifluoromethyltriiodogermane can be used to prepare the trichloride and the trifluoride.



Trifluoromethyltrifluorogermane melts at +3° C in a sealed tube, and the vapor pressures of the solid accord with the relationship

$$\log p_{\text{mm}} = 11.94 - 2451 T^{-1}.$$

These properties are similar to those of germanium tetrafluoride. Aqueous sodium hydroxide reacts at room temperature with the three CF_3GeX_3 compounds to give fluoroform. Similar behavior is shown by perfluoroalkyl derivatives of tin and lead. With cold water the CF_3GeX_3 derivatives afford stable clear solutions, although the iodo compound is not immediately miscible. On addition of potassium fluoride solution the novel salt $\text{K}_2[\text{CF}_3\text{GeF}_5]$ is produced, but unlike $\text{K}[\text{CF}_3\text{BF}_3]$ it is unstable to base.

C. Tin

Several perfluoroalkyl and polyfluoroalkyl, and a number of perfluorovinyl and pentafluorophenyl compounds of tin have been prepared (Table II). Their study has added much to our knowledge of the chemical and spectroscopic properties of fluorocarbon-metal compounds.

It was discovered independently by two groups of workers (46, 73-75) that the tin-tin bond of hexamethylditin can be cleaved by trifluoromethyl iodide according to the equation,

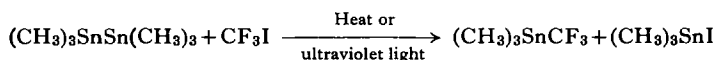


TABLE II
FLUOROCARBON COMPOUNDS OF TIN

Compound	Physical properties	Reference
$(\text{CH}_3)_3\text{SnCF}_3$	M.p., -50.9°C ; liquid, b.p. 100°C , ΔH_{vap} 8.98 kcal/mole ^a	(46, 75)
$(\text{CH}_3)_2(\text{CF}_3)\text{SnCl}$	Solid, m.p. 46°C	(75)
$(\text{CH}_3)_3\text{SnC}_2\text{F}_5$	Liquid, b.p. 107°C , ΔH_{vap} 8.52 kcal/mole ^a	(46)
$(\text{CH}_3)_2\text{Sn}(\text{C}_2\text{F}_5)_2$	Liquid, b.p. $62^\circ\text{C}/89\text{ mm}$	(29)
$(\text{C}_2\text{H}_5)_3\text{SnC}_2\text{F}_5$	Liquid, b.p. 177.4°C , ΔH_{vap} 9.36 kcal/mole ^a	(46)
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{C}_2\text{F}_5)_2$	Liquid, b.p. $42^\circ\text{C}/1\text{ mm}$	(29)
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CF}_2\text{CF}_2\text{H})_2$	Liquid, b.p. $46^\circ\text{C}/0.2\text{ mm}$	(78)
$(\text{CH}_3)_2\text{Sn}(\text{CF}_2\text{CF}_2\text{H})_2$		(78a)
$(n\text{-C}_4\text{H}_9)_3\text{SnC}_2\text{F}_5$	Liquid, b.p. $48^\circ\text{C}/0.03\text{ mm}$	(29)
$(\text{CH}_3)_3\text{SnCF}_2\text{CF}_2\text{Sn}(\text{CH}_3)_3$	Oil	(76)
$(\text{CH}_3)_2\text{Sn}(n\text{-C}_3\text{F}_7)_2$	Liquid	(9)
$(\text{C}_6\text{H}_5)_3\text{SnC}_2\text{F}_5$	Solid, m.p. 127°C	(46)
$(\text{C}_6\text{H}_5)_2\text{SnC}_2\text{F}_4$	Solid, m.p. 128°C	(76)
$(\text{CF}_2:\text{CF})_4\text{Sn}$	Liquid, b.p. $53^\circ\text{C}/19\text{ mm}$	(37)
$(\text{CH}_3)_2\text{Sn}(\text{CF}:\text{CF}_2)_2$	Liquid, b.p. $60^\circ\text{C}/40\text{ mm}$	(37)
$(\text{C}_2\text{H}_5)_2\text{Sn}(\text{CF}:\text{CF}_2)_2$	Liquid, b.p. $56^\circ\text{C}/12\text{ mm}$	(39)
$(\text{C}_2\text{H}_5)_3\text{SnCF}:\text{CF}_2$	Liquid, b.p. $66^\circ\text{C}/12\text{ mm}$	(39)
$n\text{-C}_4\text{H}_9\text{Sn}(\text{CF}:\text{CF}_2)_3$	Liquid, b.p. $44^\circ\text{C}/1.3\text{ mm}$	(39)
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CF}:\text{CF}_2)_2$	Liquid, b.p. $62^\circ\text{C}/0.4\text{ mm}$	(37)
	b.p. $53^\circ\text{C}/0.2\text{ mm}$	(39)
$(n\text{-C}_4\text{H}_9)_3\text{SnCF}:\text{CF}_2$	Liquid, b.p. $81^\circ\text{C}/0.4\text{ mm}$	(37)
	b.p. $73^\circ\text{C}/0.2\text{ mm}$	(39)
$(\text{CH}_2:\text{CH})_2\text{Sn}(\text{CF}:\text{CF}_2)_2$	Liquid, b.p. $52^\circ\text{C}/10\text{ mm}$	(37)
$\text{C}_6\text{H}_5\text{Sn}(\text{CF}:\text{CF}_2)_3$	Liquid, b.p. $60^\circ\text{C}/0.65\text{ mm}$	(39)
$(\text{C}_6\text{H}_5)_2\text{Sn}(\text{CF}:\text{CF}_2)_2$	Liquid, b.p. $77^\circ\text{C}/0.02\text{ mm}$	(37)
$(\text{C}_6\text{H}_5)_3\text{SnCF}:\text{CF}_2$	Solid, m.p. 68°C	(39)
$(\text{C}_6\text{F}_5)_4\text{Sn}$	Solid, m.p. 221°C	(77a)
$(\text{C}_6\text{F}_5)_2\text{Sn}(\text{CH}_3)_2$	Liquid	(77a)
$(\text{C}_6\text{F}_5)_3\text{SnC}_6\text{H}_5$	Solid, m.p. 102°C	(77a)
$(\text{C}_6\text{F}_5)_3\text{SnCl}$	Solid, m.p. 106°C	(77a)
$(\text{C}_6\text{F}_5)_2\text{SnCl}_2$	Liquid	(77a)

^a Data from the vapor pressure equations

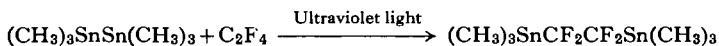
$$\log_{10}p(\text{mm}) = 8.139 - 1961 T^{-1} [(\text{CH}_3)_3\text{SnCF}_3];$$

$$\log_{10}p(\text{mm}) = 7.781 - 1863 T^{-1} [(\text{CH}_3)_3\text{SnC}_2\text{F}_5];$$

$$\log_{10}p(\text{mm}) = 7.422 - 2046 T^{-1} [(\text{C}_2\text{H}_5)_3\text{SnC}_2\text{F}_5].$$

Several $\text{R}_3\text{SnR}_\text{F}$ compounds have been made from similar reactions involving pentafluoroethyl iodide and hexaethyl- or hexaphenylditin (46).

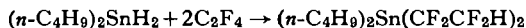
A related reaction is that between hexamethylditin and tetrafluoroethylene (76).



The compound, 1,2-bis(trimethylstannyl)tetrafluoroethane is an oil with a tendency to decompose in moist air. The white modification of diphenyltin polymer (77) reacts with tetrafluoroethylene under similar conditions to afford an adduct $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{CF}_2)_2$, a white crystalline air-stable solid of unknown molecular weight (76).

The preparation of dimethylbis(perfluoropropyl)tin by treating dimethyltin dichloride with perfluoro-*n*-propyllithium has been mentioned previously (9) (Section II). Similarly, the compounds $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{C}_2\text{F}_5)_2$, $(n\text{-C}_4\text{H}_9)_3\text{SnC}_2\text{F}_5$, and $(\text{CH}_3)_2\text{Sn}(\text{C}_2\text{F}_5)_2$ have been prepared in good yield by adding pentafluoroethyl iodide to a mixture of alkyltin chlorides and magnesium in tetrahydrofuran (29) (Section III). It is obvious from these studies that a variety of perfluoroalkyltin compounds could be obtained via perfluoroalkyllithium reagents, or by a Barbier-type procedure. However, it may be impossible to synthesize the as yet unknown tetrakis(perfluoroalkyltin)tin compounds by these methods (see Section II).

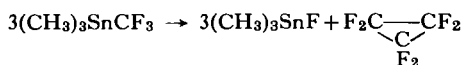
Di-*n*-butylbis(1,1,2,2-tetrafluoroethyl)tin appears to have been the first fluorocarbon-tin compound to have been reported (78). It was prepared by heating at 90° C in an autoclave a mixture of di-*n*-butyltin dihydride and tetrafluoroethylene.



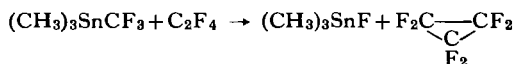
This addition reaction is, of course, similar to the reactions that occur between a variety of organotin hydrides and unsaturated compounds,⁹ and represents a potentially useful synthetic route to a variety of polyfluoroalkyltin compounds. It is, therefore, significant that equimolar quantities of tetrafluoroethylene and dimethyltin dihydride react at 25°C in the absence of solvent or catalyst to afford the hydride $(\text{CH}_3)_2\text{Sn}(\text{H})\text{C}_2\text{F}_4\text{H}$ in excellent yield. A similar reaction with a 1:2 molar ratio of the dihydride and olefin gives mainly dimethylbis(1,1,2,2-tetrafluoroethyl)tin (78a). With bromotrifluoroethylene and dimethyltin dihydride in a 1:1 molar ratio, the main reaction products are $\text{CF}_2\text{:CFH}$, $(\text{CH}_3)_3\text{SnBr}$, metallic Sn, and H_2 . In a 1:2 molar ratio $(\text{CH}_3)_2\text{Sn}(\text{C}_2\text{F}_3\text{BrH})_2$ is formed, the other main products being $(\text{CH}_3)_2\text{SnBr}_2$ and $\text{CF}_2\text{:CFH}$, but no metallic Sn is formed.

⁹ See the contribution by Kuivila in this volume.

With the exception of the phenyl derivatives, the perfluoroalkyl- and polyfluoroalkyltin compounds are all colorless liquids. The two known phenyl derivatives $(\text{C}_6\text{H}_5)_3\text{SnC}_2\text{F}_5$ and $(\text{C}_6\text{H}_5)_2\text{SnC}_2\text{F}_4$, not unexpectedly, are solids (Table II). The compounds are all thermally stable at ambient temperatures but decompose on heating above 100°C . Thus, although $(\text{CH}_3)_3\text{SnC}_2\text{F}_5$ may be heated at 100°C for 15 hours without detectable decomposition, above 180°C pyrolysis is rapid (46). A thorough study of the effect of heat on trimethylperfluoromethyltin has been made by Clark and Willis (75). The compound is stable at 100°C , but at 150°C in a sealed Pyrex tube the reaction



occurs. Traces of tetrafluoroethylene, fluoroform, and silicon tetrafluoride are also produced. The course of this decomposition evidently involves migration of a fluorine atom from the perfluoromethyl group to tin with release of a difluoromethylene radical. Perfluorocyclopropane could form by dimerization of the carbene to afford tetrafluoroethylene, followed by further reaction between difluorocarbene and the fluoroolefin. In support of this idea is the addition reaction,

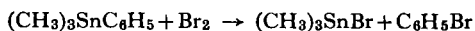


which takes place quantitatively at 150°C .

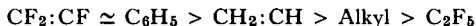
Fluoroalkyl groups are easily removed from tin by aqueous base (46, 73–75). Fluoroform is liberated quantitatively when trimethylperfluoromethyltin is treated with aqueous alkali in the cold (77). Even hot water will produce monohydro-perfluoroalkanes from the perfluoroalkyltin compounds. A similar easy hydrolysis to afford monohydro-perfluoroalkanes occurs with perfluoroalkyllead, -germanium, and -antimony compounds. Moreover, fluoroalkyl derivatives of transition metals are also very easily decomposed by aqueous alkali, but fluoroalkanes are not a principal decomposition product (Section VI).

From the reaction between trimethylperfluoromethyltin and chlorine at -50°C , dimethylperfluoromethyltin chloride is obtained as a solid having a pungent irritating odor (75). The thermal stability of $(\text{CH}_3)_2\text{CF}_3\text{SnCl}$ is low. It decomposes at 80°C , affording perfluorocyclopropane and unidentified products.

Elimination of the relatively electropositive methyl group, rather than the trifluoromethyl, during reaction with chlorine is in distinct contrast to the behavior of mixed alkyl-aryl tin compounds. With halogens the more electronegative group is removed first.



Alkyl groups are also cleaved in preference to perfluoroalkyl groups when alkylperfluoroalkyltin compounds are treated with hydrogen chloride or with boron trichloride (46). Thus trimethylperfluoromethyltin yields 80% of 2 moles of methane on warming with dry hydrogen chloride, and trimethylperfluoroethyltin reacts with gaseous boron trichloride at room temperature to give methylboron dichloride. This behavior is in distinct contrast to that of alkylperfluorovinyltin compounds, described below, which with even very weak protonic acids yield trifluoroethylene quantitatively, and with boron trichloride or boron trifluoride yield perfluorovinylboron compounds. An explanation for the difference in behavior shown by these various tin compounds towards electrophilic reagents has been advanced in terms of probable relative electron density at carbon atoms attached to tin (46). The group cleaved will be the one in which the carbon atom bonded to tin has the greatest electron density associated with it. This carbon atom may not necessarily be part of the most electronegative group. In perfluoroalkyltin compounds the inductive effect of the fluorine atoms may be such as to render the α -carbon atom of the fluorocarbon group less electron-rich than α -carbon atoms of alkyl groups. Therefore, the unfluorinated group is preferentially cleaved by electrophilic reagents. The reverse behavior of the alkylperfluorovinyltin compounds is also readily understandable. In these substances the fluoro group is bonded to tin through an sp^2 -hybridized carbon atom, not sp^3 , as in the perfluoroalkyl derivatives. The electron density of the filled π orbital of the α -carbon atom would be expected to attract the attacking electrophilic reagent, and so the perfluorovinyl group is cleaved. Whatever the true explanation for these effects, these studies have permitted an extension of the acid cleavage series of organo-groups from tin (79) to include the fluorocarbon groups C_2F_5 and C_2F_3 (29, 37):

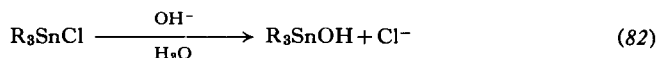
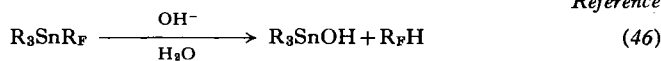


It is important to recall (Section IV, A) that the reaction between boron trifluoride and alkylperfluoroalkyltin compounds in carbon tetrachloride follows a course different from that of the reaction between gaseous boron trichloride and the alkylperfluoroalkyltin compounds. With $(\text{CH}_3)_3\text{SnCF}_3$

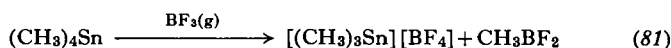
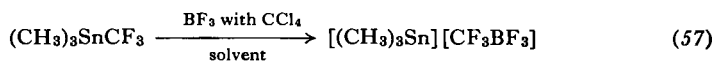
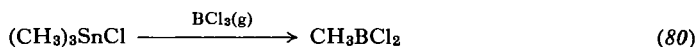
and boron trifluoride the Sn—CF₃ linkage is cleaved heterolytically, affording [(CH₃)₃Sn] [CF₃BF₃].

It will now be apparent to the reader that perfluoroalkyl groups when bonded to many metals display pseudohalogen character in their reactions, and it is worth summarizing examples of this in tin chemistry.

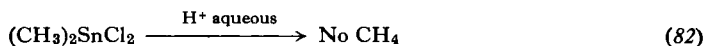
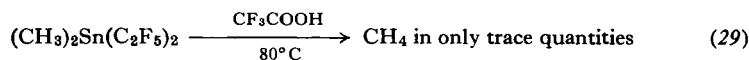
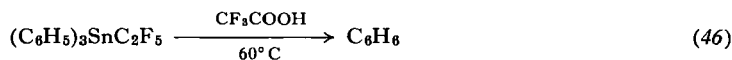
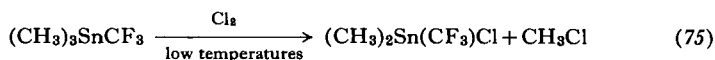
(a) *Reaction with aqueous base*



(b) *Reactions with boron halides*

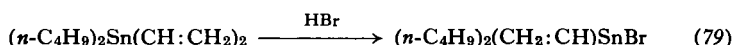
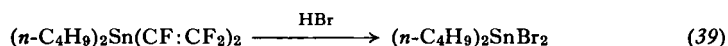
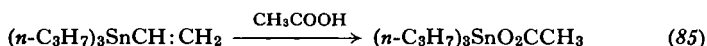
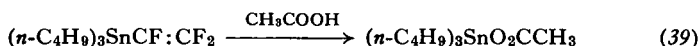
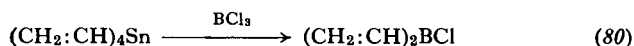
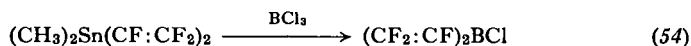
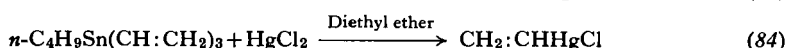
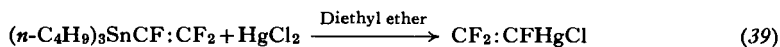
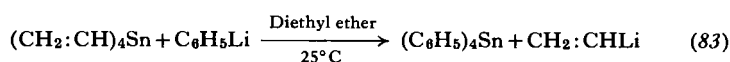
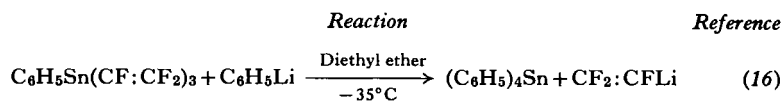


(c) *Reactions with halogens or protonic acids*



With trifluoroacetic acid at 80°C di-*n*-butylbis(pentafluoroethyl)tin yielded only about 7% of its butyl groups as butane. Under similar conditions a sample of tetra-*n*-butyltin gave butane in nearly 50% yield (29). It is evident that (*n*-C₄H₉)₂Sn(C₂F₅)₂ is more similar to (*n*-C₄H₉)₂SnCl₂ than to (*n*-C₄H₉)₄Sn.

Several perfluorovinyltin compounds (Table II) have been prepared recently (Section III), and reference has already been made to the fact that $\text{CF}_2\text{:CF-Sn}$ groups are very reactive. They are less stable thermally and kinetically than their vinyltin analogs (11). Some differences in behavior are listed in Table III, a summary of results presented elsewhere (37, 39). On the other hand, perfluorovinyl- and vinyltin compounds have a number of reactions in common; for example,



Pentafluorophenyltin compounds have recently been prepared independently by three groups of workers (19b, 57a, 77a). These fluoroaromatic derivatives of tin can be obtained by treating the appropriate tin halide with pentafluorophenyllithium or pentafluorophenylmagnesium bromide. Tetra-kispentafluorophenyltin is stable to its melting point (221°C). Pentafluorophenyltin compounds are reported (57a) to be stable in aqueous ethanol, but are rapidly hydrolyzed on addition of catalytic quantities of halide or cyanide ion, thereby releasing pentafluorobenzene. Phenyl groups are cleaved by acids more easily than the pentafluorophenyl groups from phenylpentafluorophenyltin compounds.

TABLE III

SOME CHEMICAL DIFFERENCES BETWEEN PERFLUOROVINYLTIN- AND VINYL TIN COMPOUNDS

Perfluorovinyltin compounds		Vinyltin compounds	
Reactants	Products	Reactants	Products
$(\text{CF}_2:\text{CF})_4\text{Sn} + \text{CF}_3\text{COOH}$ at 100°C	100% $\text{CF}_2:\text{CF}-\text{Sn}$ cleaved as $\text{CF}_2:\text{CFH}$	$(\text{CH}_2:\text{CH})_4\text{Sn} + \text{CF}_3\text{COOH}$ at 100°C	75% $\text{CH}_2:\text{CH}-\text{Sn}$ cleaved as $\text{CH}_2:\text{CH}_2$
$(\text{CF}_2:\text{CF})_4\text{Sn} + 20\% \text{NaOH}$ at 100°C	$\text{CF}_2:\text{CFH}$ formed quantitatively	$(\text{CH}_2:\text{CH})_4\text{Sn} + 20\% \text{NaOH}$ at 100°C	$\text{CH}_2:\text{CH}_2$ in $\sim 10\%$ yield
$(\text{CF}_2:\text{CF})_4\text{Sn} + \text{H}_2\text{O}$ at 100°C	$\sim 65\%$ yield of $\text{CF}_2:\text{CFH}$	$(\text{CH}_2:\text{CH})_4\text{Sn} + \text{H}_2\text{O}$ at 100°C	$\sim 7\%$ yield of $\text{CH}_2:\text{CH}_2$
$(\text{CF}_2:\text{CF})_4\text{Sn} + \text{dry O}_2$	Waxy white solid, probably polymer	$(\text{CH}_2:\text{CH})_4\text{Sn} + \text{dry O}_2$	No reaction
$(\text{C}_2\text{H}_5)_3\text{SnCF}:\text{CF}_2$ on standing over a prolonged period	White solid, containing C, H, F and Sn, sublimable at 155°C <i>in vacuo</i>	$(\text{C}_2\text{H}_5)_3\text{SnCH}:\text{CH}_2$ on standing over a prolonged period	No decomposition
$(\text{C}_6\text{H}_5)_2\text{Sn}-(\text{CF}:\text{CF}_2)_2 + \text{HCl(g)}$	C_6H_6 and $\text{CF}_2:\text{CFH}$ formed initially in equal amounts	$(\text{C}_6\text{H}_5)_2\text{Sn}-(\text{CH}:\text{CH}_2)_2 + \text{HCl(g)}$	C_6H_6 formed initially in greater amount than $\text{CH}_2:\text{CH}_2$
$(\text{C}_4\text{H}_9)_2\text{Sn}-(\text{CF}:\text{CF}_2)_2 + \text{anhydrous C}_2\text{H}_5\text{OH}$ and reflux	Cleavage giving $(\text{C}_4\text{H}_9)_2\text{Sn}-(\text{OC}_2\text{H}_5)_2 + \text{CF}_2:\text{CFH}$	$\text{R}_2\text{Sn}(\text{CH}:\text{CH}_2)_2 + \text{anhydrous C}_2\text{H}_5\text{OH}$	No reaction
$(\text{C}_6\text{H}_5)_3\text{SnCF}:\text{CF}_2 + (\text{C}_6\text{H}_5)_3\text{SnH}$	Cleavage giving $\text{CF}_2:\text{CFH}$ and $(\text{C}_6\text{H}_5)_6\text{Sn}_2$	$(\text{C}_6\text{H}_5)_3\text{SnCH}:\text{CH}_2 + (\text{C}_6\text{H}_5)_3\text{SnH}$	Addition giving $(\text{C}_6\text{H}_5)_3\text{Sn}-\text{CH}_2\text{CH}_2\text{Sn}-(\text{C}_6\text{H}_5)_3$
$(\text{C}_4\text{H}_9)_3\text{SnCF}:\text{CF}_2 + \text{C}_2\text{H}_5\text{ONa}$ and reflux	Cleavage giving $(\text{C}_4\text{H}_9)_3\text{SnOC}_2\text{H}_5$	$\text{R}_3\text{SnCH}:\text{CH}_2 + \text{C}_2\text{H}_5\text{ONa}$	No reaction

D. Lead

At present our knowledge of fluorocarbon-lead compounds is limited to $(\text{CH}_3)_3\text{PbCF}_3$ and $(\text{CH}_3)_3\text{PbC}_2\text{F}_5$ (46). These substances can be obtained by heating at 150°C mixtures of tetramethyllead and trifluoromethyl iodide or pentafluoroethyl iodide, respectively. Considerable quantities of fluoriform and pentafluoroethane are produced in these reactions and vapor phase chromatography was used to separate the desired lead compounds from unreacted tetramethyllead and methyl iodide.

It is worth noting that tetraalkylsilicon and tetraalkyltin compounds do not react with perfluoroalkyl iodides to give more than trace amounts of $\text{R}_3\text{MR}_\text{F}$ ($\text{M} = \text{Si}, \text{Sn}$). Presumably the temperatures required to bring about homolytic fission of alkyl-silicon or alkyl-tin bonds are so high that formation of stable $\text{R}_\text{F}-\text{Si}$ and $\text{R}_\text{F}-\text{Sn}$ groups is not possible. Thus both $(\text{CH}_3)_3\text{SnF}$ and $(\text{CH}_3)_3\text{SiF}$ have been observed from thermal reactions between trifluoromethyl iodide and the tetramethyltin and -silicon compounds. Moreover, the higher the reaction temperatures employed, the greater is the tendency for the perfluoroalkyl groups to abstract hydrogen from the alkyl groups, thereby giving perfluoroalkanes ($\text{R}_\text{F}\text{H}$). Indeed, even in the reactions involving tetramethyllead, mentioned above, copious quantities of the monohydroperfluoroalkanes are produced.

Both trimethylperfluoromethyl- and trimethylperfluoroethyllead are liquids. The vapor pressures of liquid $(\text{CH}_3)_3\text{PbC}_2\text{F}_5$ are described by the equation $\log_{10} p_{\text{mm}} = 7.843 - 2040 T^{-1}$, from whence the constants b.p. 138°C ; Trouton constant, 22.7 e.u.; and ΔH_{vap} 9.34 kcal/mole can be calculated. The chemical behavior of the perfluoroalkyllead compounds parallels that of their tin analogs.

Now that such reagents as $n\text{-C}_3\text{F}_7\text{Li}$, $\text{C}_6\text{F}_5\text{Li}$, and $\text{CF}_2:\text{CFMgBr}$ have been obtained there seems no reason why a variety of fluorocarbon-lead compounds cannot be prepared from organolead halides.¹⁰

VI

TRANSITION METAL DERIVATIVES

A. Introduction

Hydrocarbon compounds of transition metals have been known for over one hundred years, and since the discovery of ferrocene they have been

¹⁰ Very recently some pentafluorophenyllead compounds have been obtained for ^{19}F NMR studies (19b).

described in ever increasing numbers. Only recently, however, has any work been done on the synthesis and study of compounds wherein fluorocarbon groups are bonded to these metals. As in the case of the hydrocarbon complexes, the fluorocarbon derivatives are of more than one type. Because of this it is necessary to remind the reader of the different ways in which carbon atoms can be linked to transition metals. Moreover, this is relevant in attempting to understand differences between hydrocarbon-metal compounds on the one hand and the fluorocarbon-metal compounds on the other.

A transition metal can be linked to a carbon atom either through a single electron-pair bond, or through a link possessing multiple bond character. The electron-pair metal-carbon bond is analogous to that found in organo-derivatives of main group metals [e.g., $(\text{CH}_3)_4\text{Pb}$]. It is formed by overlap of two orbitals, each containing one electron, along the axis joining the two atoms. In molecular orbital terminology this is a σ bond. In the majority of known organo-transition metal compounds, however, current theory proposes multiplicity in bonds between the metal and the carbon atom. Thus in metal-carbon linkages in carbonyls, and perhaps in some cyanides, it is believed that there is not only a σ bond, involving donation of an electron pair in an sp orbital of carbon to a vacant orbital on the metal, but also a π bond. The latter can arise through overlap of a filled d or d -hybrid orbital of the metal and a vacant, or partially vacant, unhybridized p orbital of the carbon. Similarly, in the so-called " π complexes" where unsaturated hydrocarbon molecules or ions donate π electrons to form σ bonds to metals, π bonding is believed to occur through overlap of filled metal d orbitals with vacant antibonding orbitals on the hydrocarbon moieties. The π component of the bond plays an important role, because it provides a mechanism for removing electronic charge from the metal into bonding regions between the ligand and the metal, thereby strengthening the metal-carbon linkages. This strengthening by π bonding cannot operate between transition metals and the carbon atoms of alkyl groups because the latter have no low-energy vacant orbitals.

It is not surprising, therefore, that alkyl group-transition metal linkages are usually less stable than those between transition metals and the π electron donors which possess the π^* antibonding orbitals. It is less obvious, however, why alkyls of transition metals should in general be less stable¹¹ than

¹¹ The term "stability" as used by chemists in this field usually refers to the resistance of the compound to decomposition by thermal means or resistance to oxygen or to

those of the metals of the main groups of the Periodic Classification, or those of mercury.

Many of the simple alkyl transition metal complexes exist only at low temperatures and some are also extremely sensitive to air and moisture. The latter property is also found with alkyl compounds of some metals of the main groups of the Periodic Table (e.g. alkali metals), but is not found with organo-compounds of other metals such as tin. Moreover, alkyl compounds of main group metals tend to be more stable thermally than their transition metal counterparts. Several suggestions have been put forward to account for these observations.

Jaffe and Doak (86) believe that normal σ bonds involving a carbon sp^3 orbital and a suitable orbital on a transition metal are weaker than those to main group metals because they have only about one-third of the ionic resonance energy which stabilizes alkali metal alkyls and only about half the covalent energy¹² that leads to stable bonds to other main group elements and presumably to mercury as well. Following the isolation of several transition metal complexes of varying stability containing alkyl or aryl¹³ groups σ -bonded to the metals, Chatt and Shaw (87, 88) proposed that the occurrence of metal-carbon σ bonds is usually favored by the simultaneous presence on the metal of specific ligands, notably tertiary phosphines, carbonyl, and cyclopentadienyl groups, etc. These ligands are those which are believed to form π as well as σ bonds to transition metals. It was suggested that the effect of this π bonding in the complex is to enhance the energy difference between the highest energy orbital which contains electrons and the lowest energy orbital which is vacant. π Bonding lowers the energy of

moisture. Unfortunately, therefore, the observations are all too frequently of a qualitative nature. Because this field is under rapid development new compounds are being reported in large numbers but little time and effort is being spent on examining their properties in detail. Nevertheless, provided it is fully recognized that the term "stability" is being used loosely, sufficient qualitative data are available for worthwhile comparisons to be made.

¹² Calculated from terms involving overlap integral and ionization potentials of bonded atoms.

¹³ Several transition metal complexes have been prepared in which aryl groups are σ -bonded to the metals. They are often more stable than their alkyl analogs, and sometimes exist where the latter cannot be prepared. The enhanced stability could perhaps be due to the higher electronegativity of aryl groups compared with alkyl, leading to a larger ionic resonance energy in the carbon-metal σ bond, or to the possibility of π bonding between the metal's d electrons and vacant π^* orbitals of the aromatic rings. However, on the basis of the limited data available it would appear that σ bonds between aryl groups and transition metals are less robust than the bonds in comparable π complexes involving olefins, polyolefins, or aromatics.

the highest energy d orbital which contains electrons by involving these electrons in bonding. In this manner the energy required to promote the electrons into a vacant orbital of the complex as a prelude to decomposition is increased.

These ideas imply decomposition by a dissociative mechanism, a reasonable supposition for a thermal process. However, as mentioned previously, air or moisture sensitivity is also used as a criterion of stability. If this is the case it is reasonable to suppose that it is the presence of accessible orbitals either empty or only partially filled which has led to the organometallic compound's susceptibility to nucleophilic attack. Such an organometallic compound would be more easily converted to other substances by hydrolysis or oxidation, provided the products are thermodynamically more stable. Conversely, organometallics in which all the low-lying orbitals are engaged in bonding would be expected to be more resistant to chemical conversion, their stability being determined kinetically rather than thermodynamically. In this respect it is interesting to note that in the more stable organo-derivatives of the transition metals either the Sidgwick Effective Atomic Number Rule is obeyed, so that the metals have the closed shell configuration of the rare gases, or the number of electrons associated with the metals is two less than the rare gas configuration, as in the compounds $(\text{ligand})_2\text{MR}_2$ [$\text{R} = \sigma$ -bonded organo-group, $\text{M} = \text{Ni}, \text{Pd}$ or Pt]. The latter substances, however, are square planar complexes with the metals having a d^8 configuration. In terms of the ligand field theory this is a situation predicted to give rise to relatively high ligand field stabilization. Finally, it is worth remembering that unlike the situation with main group metals such as tin or lead, it is not possible to surround a transition metal with a sufficient number of alkyl or aryl groups to achieve a rare gas electron configuration. The σ -bonded groups are only one-electron donors, considering the metal in the zero-valent state. Since transition metals lack anywhere from eight ($\text{Ni}^0, 3d^8 4s^2$) to fifteen ($\text{Sc}^0, 3d^1 4s^2$) electrons to attain their Effective Atomic Number it would be sterically impossible to achieve this goal solely with σ -bonded groups.

At this stage of our knowledge of transition metal-carbon single bonds all that can be said about the factors which govern their stability is that they are many, and by no means fully understood. Clearly it will be advantageous if many other compounds containing linkages of this kind are prepared, and their chemical characteristics examined. Only in this way will the properties of single electron pair bonds between carbon atoms and transition metals be

more fully interpreted. A recent important advance has been the synthesis of a large number of compounds in which fluorocarbon groups are σ -bonded to transition metals. Less well developed at present is the chemistry of π complexes involving unsaturated fluorocarbons. The former class of substance will be reviewed first, and the π complexes will be discussed subsequently.

B. Perfluoroalkyl, Polyfluoroalkyl, Polyfluoroalkenyl, and Pentafluorophenyl Compounds

According to the ideas of Jaffe and Doak (86), mentioned in the previous section, single electron-pair bonds between carbon atoms of alkyl or aryl groups and transition metal atoms may be inherently unstable due to a relatively low ionic resonance energy. If there is any validity to this suggestion, an increase in the electronegativity difference between the transition metals and the organic groups would raise the ionic resonance energy, thus stabilizing the bonds. Clearly by substitution of hydrogen of a hydrocarbon group by fluorine, the group will become more electronegative. Perfluoroalkyl groups are very electronegative. Infrared spectroscopic studies suggest values of 3.3 (89) or 3.5 (90) on the Pauling scale¹⁴ for the electronegativity of the CF_3 group. While it may be unwise to assign a precise value to the electronegativity of CF_3 or polyfluoroalkyl groups it is well known that these groups are highly electron attracting, so that perfluoroalkyl iodides display a certain degree of pseudohalogen character (1, 2). From the foregoing considerations it became evident to at least one group of workers (91, 92) that a family of σ -bonded fluorocarbon-transition metal complexes should exist.

1. Preparation

Perfluoroalkyl, polyfluoroalkyl, fluoroalkenyl, and pentafluorophenyl transition metal compounds have been obtained by at least seven different kinds of reaction so far.

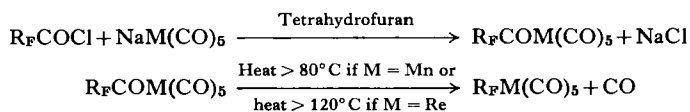
a. *Reactions between Alkali Metal Carbonylmetallates and Perfluoroacyl Halides.* It was reported (93) in 1957 that methylmanganese pentacarbonyl could be prepared via the reaction sequence,



In 1959 it was briefly mentioned (94) that $\text{CF}_3\text{Mn(CO)}_5$ could be obtained in an analogous manner. Perfluoromethylmanganese pentacarbonyl was

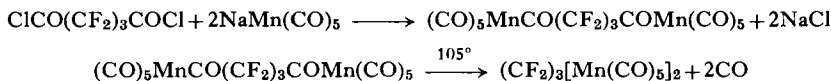
¹⁴ On this scale the electronegativity of fluorine is 4.0 and that of chlorine 3.0.

described subsequently by others (95, 96). Indeed, several other perfluoroalkylmanganese and -rhenium pentacarbonyls were reported, having been synthesized by the reactions:

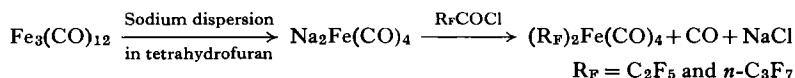


where M = Mn or Re; $\text{R}_\text{F} = \text{C}_2\text{F}_5$ (91), $n\text{-C}_3\text{F}_7$ (91, 95), $i\text{-C}_3\text{F}_7$ (95). This method has also been employed to prepare manganese pentacarbonyl derivatives of the groups $\text{Cl}(\text{CF}_2)_4-$, $\text{H}(\text{CF}_2)_4-$ (95), and $\text{H}(\text{CF}_2)_2-$ (97). In the case of the manganese compounds both the salts $\text{NaMn}(\text{CO})_5$ (91) and $\text{LiMn}(\text{CO})_5$ (95) have been used as starting materials.

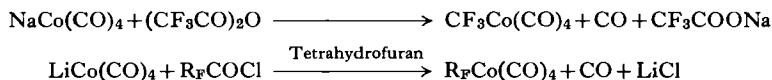
Recently $(\text{CO})_5\text{Mn}(\text{CF}_2)_3\text{Mn}(\text{CO})_5$ has been obtained via the reaction sequence (97a):



When alkali metal salts of iron carbonyl (98, 99) are treated with perfluoroacyl halides the intermediate acyl compounds are not isolated.



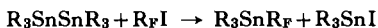
Carbon monoxide evolution and formation of perfluoroalkyl derivatives directly is also observed when alkali metal salts of cobalt carbonyl are treated with perfluoroacyl halides or anhydrides at ambient temperatures (95, 100, 101).



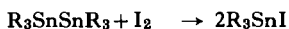
However, by carrying out these reactions below room temperature the perfluoroacylcobalt carbonyls $\text{CF}_3\text{CoCo}(\text{CO})_4$ and $\text{C}_2\text{F}_5\text{CoCo}(\text{CO})_4$ can be isolated (100, 101). It is noteworthy that the compounds $\text{CF}_3\text{CoCo}(\text{CO})_3\text{-(C}_6\text{H}_5)_3\text{P}$ and $\text{C}_2\text{F}_5\text{CoCo}(\text{CO})_3\text{(C}_6\text{H}_5)_3\text{P}$, derived from $\text{NaCo}(\text{CO})_3\text{-(C}_6\text{H}_5)_3\text{P}$, are significantly more stable toward decarbonylation, carbon monoxide evolution being observed only above 130° and 75°C , respectively (100, 101). There seems to be a growing body of evidence that it becomes increasingly difficult to convert perfluoroacyl to perfluoroalkyl derivatives when ligands other than carbon monoxide are present on the metal. Thus

$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{COC}_3\text{F}_7$ (91) and $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COC}_2\text{F}_5$ (102), somewhat air-sensitive yellow solids derived from the appropriate sodium salts and perfluoroacyl halides, have not been successfully decarbonylated.¹⁵ In view of current theories (94, 103, 104) on the nature and mechanism of decarbonylation reactions of this kind resistance to decarbonylation is perhaps due to a steric effect operating through the presence of the large $\pi\text{-C}_5\text{H}_5$ and $(\text{C}_6\text{H}_5)_3\text{P}$ ligands. In this respect the large increase in size in passing from an alkyl to a perfluoroalkyl group may also be important.

b. *Reactions of Metal Carbonyls or Their Derivatives with Perfluoroalkyl Iodides.* Iron pentacarbonyl is known to react with iodine to give iron tetracarbonyl diiodide. Because perfluoroalkyl iodides show pseudohalogen character in some of their reactions, for example the previously mentioned (Section V, C) reaction,

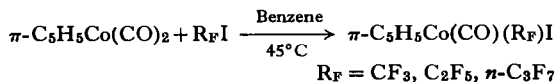
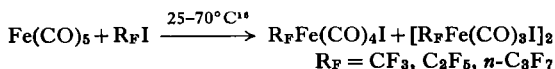


which is similar to



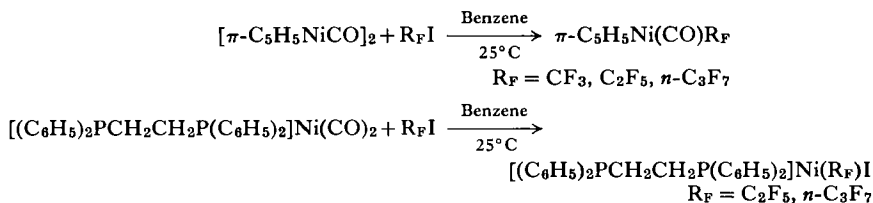
it was thought that these iodides might also react with iron pentacarbonyl. This proved to be the case, and compounds of the formulas $\text{R}_\text{F}\text{Fe}(\text{CO})_4\text{I}$ and $[\text{R}_\text{F}\text{Fe}(\text{CO})_3\text{I}]_2$ were isolated when iron pentacarbonyl and perfluoroalkyl iodides were heated under mild conditions (92, 99). The $[\text{R}_\text{F}\text{Fe}(\text{CO})_3\text{I}]_2$ compounds, dimeric by means of iodine bridges, can also be prepared from the perfluoroalkyliron tetracarbonyl iodides by heating, and this is presumably the source of the dimers in the iron pentacarbonyl reaction.

Perfluoroalkyl iodides also react with π -cyclopentadienylcobalt dicarbonyl (105), π -cyclopentadienylnickel carbonyl (102a, 106), 1,2-bis(diphenylphosphino)ethanenickel dicarbonyl (107), and di[1,2-bis(diphenylphosphino)ethane]molybdenum dicarbonyl (106) to afford perfluoroalkyl transition metal compounds.



¹⁵ Further evidence is provided by the recent observation (102b) that the perfluoro-glutaryl derivative $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CO}(\text{CF}_2)_3\text{COFe}(\text{CO})_2\text{-}\pi\text{-C}_5\text{H}_5$ is not decarbonylated on heating to 130° .

¹⁶ In early work benzene was used as solvent (92), but later studies showed that the reactions proceeded equally well in iron pentacarbonyl (99).



The relative ease of these reactions is quite surprising. Most reactions of perfluoroalkyl iodides are free radical in nature, requiring temperatures near 200°C or use of ultraviolet light. The analogy between the above reactions and those between iodine and the carbonyls further emphasizes the similarity in behavior between perfluoroalkyl iodides and halogens, particularly iodine. Thus square planar complexes $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]\text{NiI}_2$ are formed by treating 1,2-bis(diphenylphosphino)ethanenickel dicarbonyl with iodine (108). However, nickel carbonyl itself, which gives no nickel carbonyl halides with halogens, also fails to give perfluoroalkylnickel compounds with perfluoroalkyl iodides (106).

c. *Reactions of Metal Carbonyls or Their Derivatives with Tetrafluoroethylene.* Tetrafluoroethylene reacts with iron pentacarbonyl, π -cyclopentadienylcobalt dicarbonyl, and 1,2-bis(diphenylphosphino)ethanenickel dicarbonyl to give the cyclic compounds $(\text{CF}_2)_4\text{Fe(CO)}_4$ (92, 109), $\pi\text{-C}_5\text{H}_5\text{-Co(CO)(CF}_2)_4$ (110), and $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]\text{Ni(CF}_2)_4$ (106, 111). These novel compounds contain five-membered rings consisting of four CF_2 groups and the metal. It is perhaps significant that the three metal carbonyls that react with tetrafluoroethylene in this manner also react with perfluoroalkyl iodides.

Dicobalt octacarbonyl has been shown to react with tetrafluoroethylene to afford $(\text{CO})_4\text{CoCF}_2\text{CF}_2\text{Co(CO)}_4$ (112).

d. *Addition of Metal Carbonyl Hydrides to Certain Unsaturated Fluorocarbons.* Following the discovery that manganese pentacarbonyl hydride would add to tetrafluoroethylene to afford $\text{HCF}_2\text{CF}_2\text{Mn(CO)}_5$ in about 70% yield (98) a number of related reactions were reported.

Reaction	Reference
$\text{HMn(CO)}_5 + \text{CF}_2\text{:CFCI} \longrightarrow \text{HCFCICF}_2\text{Mn(CO)}_5$	(97)
$\text{HMn(CO)}_5 + \text{CF}_2\text{:CCl}_2 \longrightarrow \text{HCCl}_2\text{CF}_2\text{Mn(CO)}_5$	(97)
$\text{HMn(CO)}_5 + \text{CF}_3\text{C}\equiv\text{CCF}_3 \longrightarrow \text{trans-CF}_3\text{CH:C(CF}_3\text{)Mn(CO)}_5$	(97)
$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{H} + \text{CF}_2\text{:CF}_2 \longrightarrow \pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{CF}_2\text{CF}_2\text{H}$	(113)
$\pi\text{-C}_5\text{H}_5\text{W(CO)}_3\text{H} + \text{CF}_2\text{:CF}_2 \longrightarrow \pi\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CF}_2\text{CF}_2\text{H}$	(113)
$\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{H} + \text{CF}_2\text{:CF}_2 \longrightarrow \pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{CF}_2\text{CF}_2\text{H}$	(114)

The reaction between manganese pentacarbonyl hydride and hexafluorobut-2-yne is stereospecific, yielding principally, if not only, *trans*- $\text{CF}_3\text{CH}:\text{C}(\text{CF}_3)\text{Mn}(\text{CO})_5$ (97).

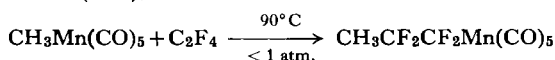
In general, the above reactions proceed under mild conditions of temperature and pressure (5–10 atm). Pentane is frequently used as solvent, the reactions being carried out in a bomb. Some of the additions, however, have been observed to proceed in Pyrex bulbs in the gas phase, at ambient temperatures and pressures less than an atmosphere (see below). Analogous reactions between metal carbonyl hydrides and nonfluorinated monoolefins to give alkyl metal carbonyls are at present unknown. However, such addition reactions account for the final products of the industrially important hydroformylation processes involving cobalt carbonyl (115). Moreover, the hydride *trans*- $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{Pt}(\text{H})\text{Cl}$ reacts with ethylene at 95°C and 40 atm to give *trans*- $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{Pt}(\text{C}_2\text{H}_5)\text{Cl}$ (116).

In the addition of transition metal hydrides to unsaturated fluorocarbons reaction proceeds best with tetrafluoroethylene. So far most of the studies have been carried out with manganese pentacarbonyl hydride. By addition of this hydride to the double bonds of either chlorotrifluoroethylene or 1,1-dichloro-2,2-difluoroethylene two isomeric products are possible. When reactions are carried out at pressures of 5 atm or greater the products are very largely the isomers $\text{HCFCICF}_2\text{Mn}(\text{CO})_5$ and $\text{HCCl}_2\text{CF}_2\text{Mn}(\text{CO})_5$, respectively. The presence of the CF_2 group adjacent to manganese was established by bromine cleavage, and by NMR studies described below. Interestingly, the direction of addition of manganese pentacarbonyl hydride to the two chlorofluoroethylenes is pressure dependent. At a little above room temperature, with ultraviolet light used to assist reaction and with the pressure at 1–2 atm, manganese pentacarbonyl hydride and chlorotrifluoroethylene afford a mixture of $\text{HCFCICF}_2\text{Mn}(\text{CO})_5$ and $\text{HCF}_2\text{CFCIMn}(\text{CO})_5$ in which the latter isomer predominates (117). These two isomers have been separated by chromatography. It would appear that two mechanisms may be operative in the reactions of manganese pentacarbonyl hydride with the chlorofluoroethylenes; i.e., a free radical mechanism and a four-center mechanism.

There appear to be limitations on the extent to which reactions between transition metal hydrides and fluoroolefins can be used to make σ -bonded fluorocarbon-metal compounds. Unsuccessful attempts have been made to add manganese pentacarbonyl hydride to 1,1-difluoroethylene, 1-chloro-2,2-difluoroethylene, perfluoropropene, and perfluoro-2-butene under con-

ditions in which the hydride adds readily to tetrafluoroethylene. It is possible that these reactions might be made to yield products by changing the conditions. This also applies to the failure to obtain products by treating π -cyclopentadienylmolybdenum, or -tungsten tricarbonyl hydrides with chlorofluoroethylenes. A further difficulty lies in the thermal instability of many of the transition metal hydrides which sometimes decompose before addition to the fluoroolefin can occur. In this connection some recent studies of reactions between tetrafluoroethylene and transition metal compounds other than hydrides may point the way to useful preparative routes to interesting compounds.

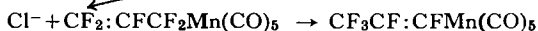
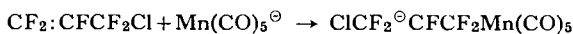
Methylmanganese pentacarbonyl reacts with tetrafluoroethylene according to the equation (117),



Phenylmanganese pentacarbonyl and tetrafluoroethylene near 100°C afford $\text{C}_6\text{H}_5\text{CF}_2\text{CF}_2\text{Mn}(\text{CO})_5$, but the yield (5–10%) is low. Studies also showed that methylmanganese pentacarbonyl does not add to chlorotrifluoroethylene below about 90° , at which temperature the desired product is unstable. These observations prompted examination of the effect of ultra-violet light on these reactions. It was found that $\text{CH}_3\text{CF}_2\text{CF}_2\text{Mn}(\text{CO})_5$ is formed quantitatively by irradiation of mixtures of methylmanganese pentacarbonyl and tetrafluoroethylene at 1–2 atm pressure. Under the same conditions methylmanganese carbonyl and chlorotrifluoroethylene afford mainly $\text{CH}_3\text{CF}_2\text{CFCIMn}(\text{CO})_5$ (30% yield) with a small amount of the isomer $\text{CH}_3\text{CFCICF}_2\text{Mn}(\text{CO})_5$.

It is probable that this type of reaction can be extended to other fluoroolefins and organometal carbonyls. Similarly the compound $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{Pt}(\text{C}_2\text{F}_5)_2$ has been obtained by treating $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{PtF}_2$ with tetrafluoroethylene in anhydrous hydrogen fluoride at 150°C (118). Reaction between perfluoroolefins or perfluoroacetylenes and phosphine-metal fluorides may be quite general, leading to other fluorocarbon derivatives of the transition metals.

e. *Reactions between Alkali Metal Carbonylmetallates and Perfluoroallyl Chloride.* Lithium (95) or sodium (91) pentacarbonylmanganate(–1) react with perfluoroallyl chloride in tetrahydrofuran to give a compound of molecular formula $\text{C}_3\text{F}_5\text{Mn}(\text{CO})_5$. Preliminary spectroscopic studies showed that this substance was the perfluoropropenyl derivative $\text{CF}_3\text{CF}:\text{CFMn}(\text{CO})_5$ (91, 95), and a subsequent study (119) established that it was formed predominantly, if not exclusively, as the *trans* isomer.



In a similar manner, the salt $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ reacts with perfluoroalkyl chloride to give *trans*- $\text{CF}_3\text{CF}:\text{CFFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (99). Treatment of the potassium salt of the anion $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]^-$ with perfluoroalkyl chloride in tetrahydrofuran, however, affords a mixture of the compounds *trans*- $\text{CF}_3\text{CF}:\text{CFNi}(\text{CO})(\pi\text{-C}_5\text{H}_5)$ and $\text{CF}_2:\text{CFCF}_2\text{Ni}(\text{CO})(\pi\text{-C}_5\text{H}_5)$ in which the latter predominates (102a).

f. *Cleavage of Alkyl-Metal Bonds with Perfluoroalkyl Iodides.* As yet only limited studies have been made on reactions of this type but preliminary results suggest that this might be a useful route to perfluoroalkyl metal compounds. From the reaction between equivalent amounts of dimethyl(bipyridyl)palladium and heptafluoro-*n*-propyl iodide in tetrahydrofuran at room temperature it is possible to isolate perfluoro-*n*-propyl(methyl)(bipyridyl)palladium. Moreover, if dimethyl(bipyridyl)palladium is treated with a large excess of heptafluoro-*n*-propyl iodide, under the same conditions as those mentioned above, bisheptafluoro-*n*-propyl(bipyridyl)palladium can be isolated (120). Formation of a significant amount of ethane was observed in this reaction but no methyl iodide was found in the reaction products. This is interesting because dimethyl(bipyridyl)palladium was observed to react with iodine to give bipyridylpalladium diiodide and methyl iodide. This is the normal behavior for methyl groups bonded to palladium (121). It would appear that the reaction between dimethyl(bipyridyl)palladium and heptafluoro-*n*-propyl iodide is more complicated than that involving this palladium compound and iodine. Moreover, at -78°C tetramethyltitanium and trifluoromethyl iodide are reported to give trimethyltitanium iodide and methane. No perfluoromethyltitanium, or for that matter any fluorine-containing compound, was isolated (121a). This is surprising.

Another example of the cleavage of an alkyl group from a transition metal by heptafluoro-*n*-propyl iodide is provided by the reaction of this iodide with $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$ which yields $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{n-C}_3\text{F}_7$ (122).

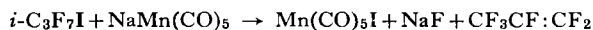
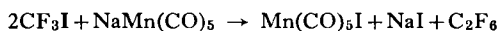
g. *Reactions between Perfluoroalkyl, Perfluoroaryl, or Perfluoroalkenyl Grignard or Lithium Reagents and Transition Metal Halides.* As described earlier in this review, it is now possible to prepare such reagents as $\text{n-C}_3\text{F}_7\text{Li}$, $\text{C}_6\text{F}_5\text{MgBr}$, and $\text{CF}_2:\text{CFLi}$. It seems probable that under carefully chosen conditions these or similar reagents will react with transition metal carbonyl

halides, π -cyclopentadienylmetal halides, or related halides to give fluorocarbon derivatives of the transition metals. As yet relatively few studies on such syntheses have been made, both because fluorocarbon-Grignard and -lithium reagents are relatively new and because it had not been realized that σ -bonded fluorocarbon-transition metal compounds would exist. When studies of the type here suggested are carried out it is likely that some unexpected results will be obtained. An indication of this is provided by an experiment involving perfluorovinylmagnesium bromide and π -cyclopentadienylnickel carbonyl iodide (102a, 123). When the products of this reaction are treated with triphenylphosphine, the compound σ -perfluorobutadienyl- π -cyclopentadienyl(triphenylphosphine)nickel can be isolated. Presumably formation of π -C₅H₅Ni(CO)CF:CF₂ is the first step of this reaction; the perfluorovinyl derivative then reacts further with the Grignard reagent with elimination of fluoride ion. Addition of triphenylphosphine displaces carbon monoxide and leads to the isolation of π -C₅H₅Ni[(C₆H₅)₃P]-(σ -CF:CFCF:CF₂). The reaction of the perfluorovinylmagnesium bromide with the Ni—CF:CF₂ group is somewhat similar to that between trimethylperfluorovinylsilane and vinyl lithium to give (CH₃)₃SiCF:CFCH:CH₂ (Section V, A).

In contrast to the unexpected product obtained from π -C₅H₅Ni(CO)I and perfluorovinylmagnesium bromide, treatment of certain transition metal halide complexes with pentafluorophenyllithium affords the expected pentafluorophenyl derivatives. In this way compounds such as (π -C₅H₅)₂Ti(C₆F₅)₂, (π -C₅H₅)₂Ti(C₆F₅)Cl, C₆F₅Fe(CO)₄I, and C₆F₅Mn(CO)₅ have been characterized (19c).

In concluding this section concerned with the preparation of σ -bonded fluorocarbon-metal compounds it is pertinent to mention two reactions which might have given the desired compounds but which in practice do not.

Reaction between trifluoromethyl iodide and manganese pentacarbonyl hydride occurs readily even below room temperature to afford manganese pentacarbonyl iodide and trifluoromethane (124). Perfluoromethylmanganese pentacarbonyl is not produced. Similarly, although perfluoroalkyl iodides and sodium pentacarbonylmanganate(−1) react, perfluoroalkylmanganese pentacarbonyls are not obtained (95, 100).



Evidently the course of these reactions is governed by the positive character of the iodine in the perfluoroalkyl iodide.

2. Properties

Known σ -bonded fluorocarbon-transition metal compounds are listed in Table IV, while perfluoroacyl derivatives are given in Table V. Although the compounds in Table IV involve many different fluorocarbon groups and different metals, the great increase in our knowledge of hydrocarbon derivatives of the transition metals during recent years must mean that countless *fluorocarbon* derivatives remain to be discovered. The fluorocarbon-metal compounds (Table IV) vary greatly in appearance. They can be solids or liquids at ambient temperatures; a few are colorless but most are colored, ranging from pale yellow, through yellow, orange, red, brown, and green to black. In general they display a high degree of volatility, as high as that of their alkyl analogs where these are known. Polyfluoro- or perfluoro-alkylmanganese pentacarbonyls sublime away slowly even at atmospheric pressure, while the red liquids π -C₅H₅Ni(CO)R_F will slowly distill at room temperature in a high vacuum system. A high degree of volatility is not surprising since this is a characteristic of organofluorine compounds.

Frequently, fluorocarbon-metal compounds are known where the comparable alkyl or aryl derivatives are not. To some extent this may be because no serious attempts have been made to prepare the particular alkyl or aryl metal compounds, thus making them unavailable for comparison purposes. However, in many instances either unsuccessful attempts at synthesis have been made, or the hydrocarbon derivative is known but is thermally much less stable than the fluorocarbon analog. At the time of writing much less common are situations where a σ -bonded alkyl transition metal group is thermally as robust as the analogous σ -bonded fluorocarbon-transition metal group.

Some comparisons of thermal stability will now be made but the reader should remember that these are frequently based on observations of a qualitative nature. The compounds HCF₂CF₂Mn(CO)₅ and C₂F₅Mn(CO)₅ decompose above 120° C whereas the existence of C₂H₅Mn(CO)₅ has not been proved; CF₃Co(CO)₄ does not decompose even when distilled at its normal boiling point (91° C), yet CH₃Co(CO)₄ and other alkylcobalt tetracarbonyls are stable only at subzero temperatures; (C₂F₅)₂Fe(CO)₄ decomposes only near 100° C, whereas (C_nH_{2n+1})₂Fe(CO)₄ compounds are unknown, even though serious attempts have been made to prepare them. The

TABLE IV
σ-BONDED FLUOROCARBON DERIVATIVES OF THE TRANSITION METALS

Compound ^a	Color and melting point (° C)	Reference
(π -C ₅ H ₅) ₂ Ti(C ₆ F ₅) ₂	Orange, m.p. 228°	(19c)
(π -C ₅ H ₅) ₂ Ti(C ₆ F ₅)Cl	Orange, m.p. 201°	(19c)
(π -C ₅ H ₅) ₂ Ti(C ₆ F ₅)F	Yellow, decomp. 240°	(19c)
(π -C ₅ H ₅) ₂ Ti(C ₆ F ₅)OH	Yellow, m.p. 183°	(19c)
HCF ₂ CF ₂ Mo(CO) ₃ (π -C ₅ H ₅)	Yellow, m.p. 53°	(98, 113)
η -C ₃ F ₇ Mo(CO) ₃ (π -C ₅ H ₅)	Orange	(122)
HCF ₂ CF ₂ W(CO) ₃ (π -C ₅ H ₅)	Yellow, m.p. 65°	(113)
CF ₃ Mn(CO) ₅	White, m.p. 82°	(95, 96)
C ₂ F ₅ Mn(CO) ₅ ^b	Liquid, f.p. 16°	(91)
η -C ₃ F ₇ Mn(CO) ₅	Liquid, f.p. 0°	(91, 95)
i -C ₃ F ₇ Mn(CO) ₅	Liquid, f.p. 2°	(95)
HCF ₂ CF ₂ Mn(CO) ₅	White, m.p. 31°	(97, 98)
H(CF ₂) ₄ Mn(CO) ₅	Colorless liquid	(95)
Cl(CF ₂) ₄ Mn(CO) ₅	Pale yellow liquid	(95)
(CF ₂) ₃ [Mn(CO) ₅] ₂	White, m.p. 161°	(97a)
HCFCICF ₂ Mn(CO) ₅	White, m.p. 43°	(97)
HCF ₂ CFCIMn(CO) ₅	White, m.p. 51°	(117)
HCCl ₂ CF ₂ Mn(CO) ₅	Pale yellow, m.p. 69°	(97)
CH ₃ CF ₂ CF ₂ Mn(CO) ₅	Pale yellow, m.p. 41°	(117)
CH ₃ CF ₂ CFCIMn(CO) ₅	Pale yellow, m.p. 52°	(117)
C ₆ H ₅ CF ₂ CF ₂ Mn(CO) ₅	White, m.p. 36°	(117)
CF ₃ CF:CFMn(CO) ₅	White, m.p. 71°	(91, 95, 119)
CF ₃ CH:C(CF ₃)Mn(CO) ₅	Yellow liquid	(97)
C ₆ F ₅ Mn(CO) ₅	White, m.p. 118°	(19c)
C ₂ F ₅ Re(CO) ₅	Very pale yellow, m.p. 39°	(91)
η -C ₃ F ₇ Re(CO) ₅	Pale yellow, m.p. 27°	(91)
CF ₃ Fe(CO) ₄ I	Orange-red, decomp. 91°	(99)
C ₂ F ₅ Fe(CO) ₄ I	Dark red, m.p. 15°	(99)
[C ₂ F ₅ Fe(CO) ₃ I] ₂	Orange-red, decomp. 110°	(99)
η -C ₃ F ₇ Fe(CO) ₄ I	Orange-red, m.p. 69°	(92, 99)
[η -C ₃ F ₇ Fe(CO) ₃ I] ₂	Pale orange, decomp. 140°	(99)
η -C ₃ F ₇ Fe(CO) ₃ [(C ₆ H ₅) ₃ PI]	Amber-brown, m.p. 125°	(125)
η -C ₃ F ₇ Fe(py) ₂ (CO) ₂ I	Brown, m.p. 123°	(125)
η -C ₃ F ₇ Fe(bipy)(CO) ₂ I	Yellow-orange, decomp. 195°	(125)
η -C ₃ F ₇ Fe(diphos)(CO) ₂ I	Brown, m.p. 110°	(126)
(CF ₂) ₄ Fe(CO) ₄	White, m.p. 77°	(92, 109)
(CF ₂) ₄ Fe(diphos)(CO) ₂	Cream colored, m.p. 229°	(126)
(C ₂ F ₅) ₂ Fe(CO) ₄	Very pale yellow, m.p. 62°	(98, 99)
(HCF ₂ CF ₂) ₂ Fe(CO) ₄	Very pale yellow, m.p. 49°	(106)

Continued

TABLE IV (continued)

Compound ^a	Color and melting point (° C)	Reference
(π -C ₃ F ₇) ₂ Fe(CO) ₄	Very pale yellow, m.p. 89°	(98, 99)
(π -C ₃ F ₇) ₂ Fe(py) ₂ (CO) ₂	Yellow-brown, m.p. 138°	(125)
(π -C ₃ F ₇) ₂ Fe(bipy)(CO) ₂	Light brown, decomp. 195°	(125)
CF ₃ CF:CFFe(CO) ₂ (π -C ₅ H ₅)	Yellow-orange, m.p. 70°	(99, 119)
C ₆ F ₅ Fe(CO) ₄ I	Red, m.p. 74°	(19c)
CF ₃ Co(CO) ₄	Light amber liquid, f.p. 11° b.p. 91° (760 mm)	(95)
C ₂ F ₅ Co(CO) ₄	Light amber liquid, b.p. 110° (760 mm)	(95, 101)
n -C ₃ F ₇ Co(CO) ₄	Light amber liquid, b.p. 44°/16 mm	(95, 101)
n -C ₇ F ₁₅ Co(CO) ₄	Yellow, m.p. 30°	(101)
CF ₃ Co(CO) ₃ [(C ₆ H ₅) ₃ P]	Pale yellow, m.p. 168°	(100)
C ₂ F ₅ Co(CO) ₃ [(C ₆ H ₅) ₃ P]	Pale yellow, m.p. 145°	(101)
C ₂ F ₅ Co(CO) ₃ [(C ₆ H ₅) ₃ As]	Dark yellow, m.p. 134°	(101)
C ₂ F ₅ Co(CO) ₃ [(C ₆ H ₅) ₃ Sb]	Yellow-brown, m.p. 120°	(101)
C ₂ F ₅ Co[(C ₆ H ₅) ₃ P](NO) ₂	Violet-brown, m.p. 65°	(101)
(CO) ₄ CoCF ₂ CF ₂ Co(CO) ₄	Orange, m.p. 80°	(112)
CF ₃ Co(CO)(π -C ₅ H ₅)I	Black, decomp. 145°	(105)
C ₂ F ₅ Co(CO)(π -C ₅ H ₅)I	Black, m.p. 138°	(105)
n -C ₃ F ₇ Co(CO)(π -C ₅ H ₅)I	Black, m.p. 121°	(105)
(CF ₂) ₄ Co(CO)(π -C ₅ H ₅)	Pale yellow, m.p. 106°	(110)
C ₂ F ₅ Ni(diphos)I	Red-brown, decomp. 260°	(107)
n -C ₃ F ₇ Ni(diphos)I	Red-brown, m.p. 220°	(107)
(CF ₂) ₄ Ni(diphos)	Yellow, decomp. ~ 245°	(106, 111)
CF ₃ Ni(CO)(π -C ₅ H ₅)	Red liquid	(102a, 106)
C ₂ F ₅ Ni(CO)(π -C ₅ H ₅)	Red-purple liquid	(102a, 106)
C ₂ F ₅ Ni[(C ₆ H ₅) ₃ P](π -C ₅ H ₅)	Dark green, m.p. 164°	(102a, 106)
n -C ₃ F ₇ Ni(CO)(π -C ₅ H ₅)	Red-purple liquid	(102a, 106)
CF ₂ :CFNi(CO)(π -C ₅ H ₅)	Red liquid	(106, 123)
C ₃ F ₅ Ni(CO)(π -C ₅ H ₅) ^c	Deep red liquid	(102a, 106)
CF ₂ :CFCF:CFNi[(C ₆ H ₅) ₃ P] (π -C ₅ H ₅)	Dark green, m.p. 114°	(106, 123)
(π -C ₃ F ₇) ₂ Pd(bipy)	Pale yellow, m.p. 180°	(120)
(π -C ₃ F ₇)Pd(CH ₃)(bipy)	Yellow, m.p. 206°	(120)
(C ₂ F ₅) ₂ Pt[(C ₆ H ₅) ₃ P] ₂	Dark green	(118)

^a In this table py = pyridine; bipy = bipyridyl; diphos = 1,2-bis(diphenylphosphino)ethane.

^b Vapor pressures over the range 80–120° C correspond to the equation $\log_{10} p(\text{mm}) = 9.100 - 2622/T^{-1}$, implying an extrapolated boiling point of 155° C (91).

^c The σ -C₃F₅—Ni group is present in this compound as a mixture of *trans*-CF₃CF:CF—Ni and CF₂:CFCF₂—Ni.

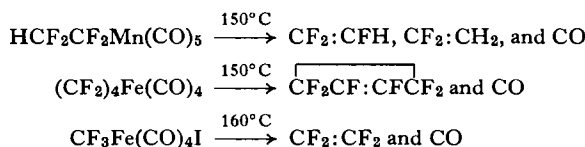
TABLE V
PERFLUOROACYL DERIVATIVES OF TRANSITION METALS

Compound	Color and melting point (° C)	Reference
$\text{CF}_3\text{COMn}(\text{CO})_5$	Pale yellow, m.p. 55°	(95, 96)
$\text{C}_2\text{F}_5\text{COMn}(\text{CO})_5$	Very pale yellow, m.p. 49°	(91)
$n\text{-C}_3\text{F}_7\text{COMn}(\text{CO})_5$	Pale yellow, m.p. 39°	(91, 95)
$i\text{-C}_3\text{F}_7\text{COMn}(\text{CO})_5$	Pale yellow, m.p. 36°	(95)
$\text{HCF}_2\text{CF}_2\text{COMn}(\text{CO})_5$	White, m.p. 47°	(97)
$(\text{CO})_5\text{MnCO}(\text{CF}_2)_3\text{COMn}(\text{CO})_5$	Pale yellow, m.p. 105°	(97a)
$\text{H}(\text{CF}_2)_4\text{COMn}(\text{CO})_5$	Pale yellow, m.p. 22°	(95)
$\text{Cl}(\text{CF}_2)_4\text{COMn}(\text{CO})_5$	Pale yellow, m.p. 39°	(95)
$\text{C}_2\text{F}_5\text{CRe}(\text{CO})_5$	Very pale yellow, m.p. 82°	(91)
$n\text{-C}_3\text{F}_7\text{CRe}(\text{CO})_5$	Pale yellow, m.p. 54°	(91)
$\text{CF}_3\text{COCO}(\text{CO})_4$	Liquid, f.p. 4°	(100)
$\text{C}_2\text{F}_5\text{COCO}(\text{CO})_4$	Liquid, f.p. -33°	(101)
$\text{CF}_3\text{COCO}(\text{CO})_3[(\text{C}_6\text{H}_5)_3\text{P}]$	Yellow, m.p. 172°	(100)
$\text{C}_2\text{F}_5\text{COCO}(\text{CO})_3[(\text{C}_6\text{H}_5)_3\text{P}]$	Yellow, m.p. 138°	(101)
$n\text{-C}_3\text{F}_7\text{COMo}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)$	Yellow, m.p. ~ 20°	(91)
$n\text{-C}_2\text{F}_5\text{COFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$	Yellow, m.p. 53°	(102)
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CO}(\text{CF}_2)_3\text{COFe}(\text{CO})_2\text{-}\pi\text{-C}_5\text{H}_5$	Orange, m.p. 112°	(102b)

nickel complexes $\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})\text{R}_F$ are all indefinitely stable *in vacuo* at ambient temperatures, but $\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})\text{CH}_3$ has only a transient existence under the same conditions. These are all examples, and there are many others, where there is clearly an enhancement in thermal stability in passing from the group $-\text{CH}_2-\text{M}$ to the group $-\text{CF}_2-\text{M}$ (M = transition metal). Such a rise in thermal stability is in agreement with simple theoretical considerations discussed earlier. The highly electronegative fluorocarbon groups should raise the ionic resonance energy of the metal-carbon σ bonds. Alternatively it is possible to explain the observations of relative thermal stability in terms of relative charge transfer. It was mentioned previously that alkyl groups cannot accept electrons from transition metals by π bonding, a process which is believed to enhance the stability of linkages between certain other ligands and transition metals. Perfluoro- and polyfluoroalkyl groups similarly cannot partake in π bonding, but their high electronegativity would lead to much less charge transfer to the metals in the σ bonds. There is some spectroscopic evidence for this (Section VIII, B), and it might well result in enhanced stability since the relatively electropositive metals

would not be required to absorb as much negative charge as when alkyl groups are ligands. It is naive, however, to expect that relative thermal stabilities can be accounted for completely satisfactorily in terms of charge transfer or resonance energy. Moreover, the stability differences are not always as evident as the above examples would suggest. For example, there seems to be little difference between the thermal stabilities of $\pi\text{-C}_5\text{H}_5\text{-Mo(CO)}_3\text{CF}_2\text{CF}_2\text{H}$ and $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{C}_2\text{H}_5$; the latter decomposes near 80°C while the former decomposes near 100°C . It has been mentioned previously that certain ligands stabilize transition metal-carbon σ bonds. It is probable that the magnitude of such stabilization will vary with the ligands and possibly be different with hydrocarbon groups than with fluoro-carbon groups. Thus in the molybdenum compounds just mentioned the cyclopentadienyl group might be more effective in stabilizing the $\text{Mo-C}_2\text{H}_5$ linkage than the $\text{Mo-CF}_2\text{CF}_2\text{H}$ linkage. Steric and other effects might also be important.

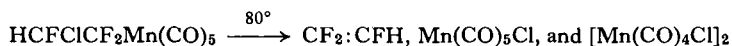
It is possible, although by no means certain, that alkyl and fluoroalkyl transition metal compounds decompose thermally by somewhat similar mechanisms. Unfortunately little is known about the decomposition products of alkyl transition metal compounds but it has been suggested that an equilibrium exists between an alkyl metal compound, where the alkyl group is an ethyl group or higher homolog, and a mixture of the metal hydride and an olefin, which is increasingly favored at higher temperatures (115, 127).¹⁷ This would imply that the decomposition involves transfer of a hydrogen atom from the organic group to the metal with release of an olefin.¹⁸ Similarly, when a perfluoro- or polyfluoroalkyl transition metal compound is heated to a sufficiently high temperature, a fluorine atom migrates with release of a fluoroolefin (92, 97, 99):



¹⁷ In ref. (127) *alkylcobalt tetracarbonyls* are specified rather than the more general term *alkyl metal compound* used by us. However, there seems to be no reason why for the sake of discussion the suggested equilibrium proposed for alkylcobalt tetracarbonyls might not be extended to include alkyl transition metal compounds as a whole.

¹⁸ The reverse reaction is believed to occur in the hydroformylation reaction (115, 127, 128) and, moreover, the reaction $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{Pt(H)Cl} + \text{C}_2\text{H}_4 \rightleftharpoons [(\text{C}_2\text{H}_5)_3\text{P}]_2\text{Pt(C}_2\text{H}_5)\text{Cl}$ is known to be reversible (116).

The temperatures quoted are those at which decomposition becomes appreciably rapid. Presumably metal fluorides are also formed in these decompositions but this has not been proven. A reaction which is apparently the reverse of these pyrolyses was mentioned above, namely the addition of platinum-fluorine bonds to tetrafluoroethylene (118). The thermal decomposition of perfluoroalkyl and polyfluoroalkyl derivatives of main group elements such as boron, silicon, or tin was mentioned in earlier sections of this chapter. Transfer of fluorine atoms from the side chains on heating was also a characteristic property. However, it is interesting to compare the reaction (97),



with the pyrolysis of $\text{HCFCICF}_2\text{SiCl}_3$ which affords CHF:CFCl (67).

Pentafluorophenyl derivatives of transition metals appear, from preliminary results (19c), to be thermally even more robust than the perfluoroalkylmetal complexes. Thus samples of pentafluorophenylmanganese pentacarbonyl are undecomposed after heating *in vacuo* at 138°C, and pyrolysis at 160°C causes only about 20% decomposition. This is to be compared with perfluoroethylmanganese pentacarbonyl which decomposes rapidly at 120–150°C, and phenylmanganese pentacarbonyl which decomposes at 100°C. The titanium compound $(\pi\text{-C}_5\text{H}_5)_2\text{Ti(C}_6\text{F}_5)_2$ is thermally stable *in vacuo* at 110°C, but pyrolysis at 150°C affords $(\pi\text{-C}_5\text{H}_5)_2\text{Ti(C}_6\text{F}_5)\text{F}$.

The great majority of the compounds listed in Table IV are stable in air, but when dissolved in organic solvents the resulting solutions are sometimes decomposed. For example, after standing for a few hours in the presence of moist air, dichloromethane solutions of perfluoroalkyliron tetracarbonyl iodides are appreciably affected (99).

Unlike fluorocarbon derivatives of main group elements, the compounds listed in Table IV do not yield fluorocarbons quantitatively on treatment with aqueous bases, although at elevated temperatures small quantities are frequently observed. With aqueous acids the fluorocarbon-transition metal complexes also produce fluorocarbons, but only in small amounts. Because of this it was incorrectly believed that the fluorocarbon-metal groups were largely unaffected by base or by acid, although considerable quantities of carbon monoxide were obtained from those compounds having metal carbonyl groups. Closer examination of these reactions showed that in very strongly basic solutions the fluoroalkyl metal groups are degraded with

rupture of the C—F bonds, forming fluoride ion in solution (97). Formation of carbonate ion was also observed.

Perfluoroalkyl and polyfluoroalkyl metal carbonyls undergo an unusual reaction with hydrogen chloride gas in Pyrex vessels (97). Above 70° C the compound $\text{HCF}_2\text{CF}_2\text{Mn}(\text{CO})_5$ affords silicon tetrafluoride in amount approximately equivalent to 50% of the fluorine content of the starting material. Carbon monoxide is also produced, but no 1,1,2,2-tetrafluoroethane is observed. Similarly, although bis(perfluoroethyl)iron tetracarbonyl does not react with hydrogen chloride gas at ambient temperatures, at 90° C small amounts of pentafluoroethane are obtained, while at 100° C or above appreciable quantities of silicon tetrafluoride are formed along with pentafluoroethane. It would appear that hydrogen fluoride must be an intermediate in the processes which yield silicon tetrafluoride when carried out in glass bulbs.

Whatever the mechanisms of the degradation reactions which result in formation of fluoride or carbonate ions, or silicon tetrafluoride, cleavage of the M—CF₂ groups is not the first step. If this were the case, fluorocarbons would be produced and the major products would have to be accounted for in terms of degradation of a fluorocarbon. Pentafluoroethane and related fluorocarbons are known, however, not to react with aqueous base or hydrogen chloride. The small amounts of fluorocarbons formed in some of these reactions suggest that conventional cleavage of M—CF₂ occurs only to a slight extent. The unsaturated compound *trans*-CF₃CH:C(CF₃)Mn(CO)₅, however, reacts with aqueous acids to give *trans*-CF₃CH:CHCF₃ quantitatively (97). Cleavage of the organic group in this manner is similar to the effect of acids on vinyl metal compounds in general (10, 11). A conventional cleavage of the fluorocarbon groups also occurs when pentafluorophenyl transition metal complexes are heated with hydrogen chloride gas. Thus at 150° C hydrogen chloride and bis(cyclopentadienyl)bis(pentafluorophenyl)-titanium afford pentafluorophenylbenzene in 80–90% yield.

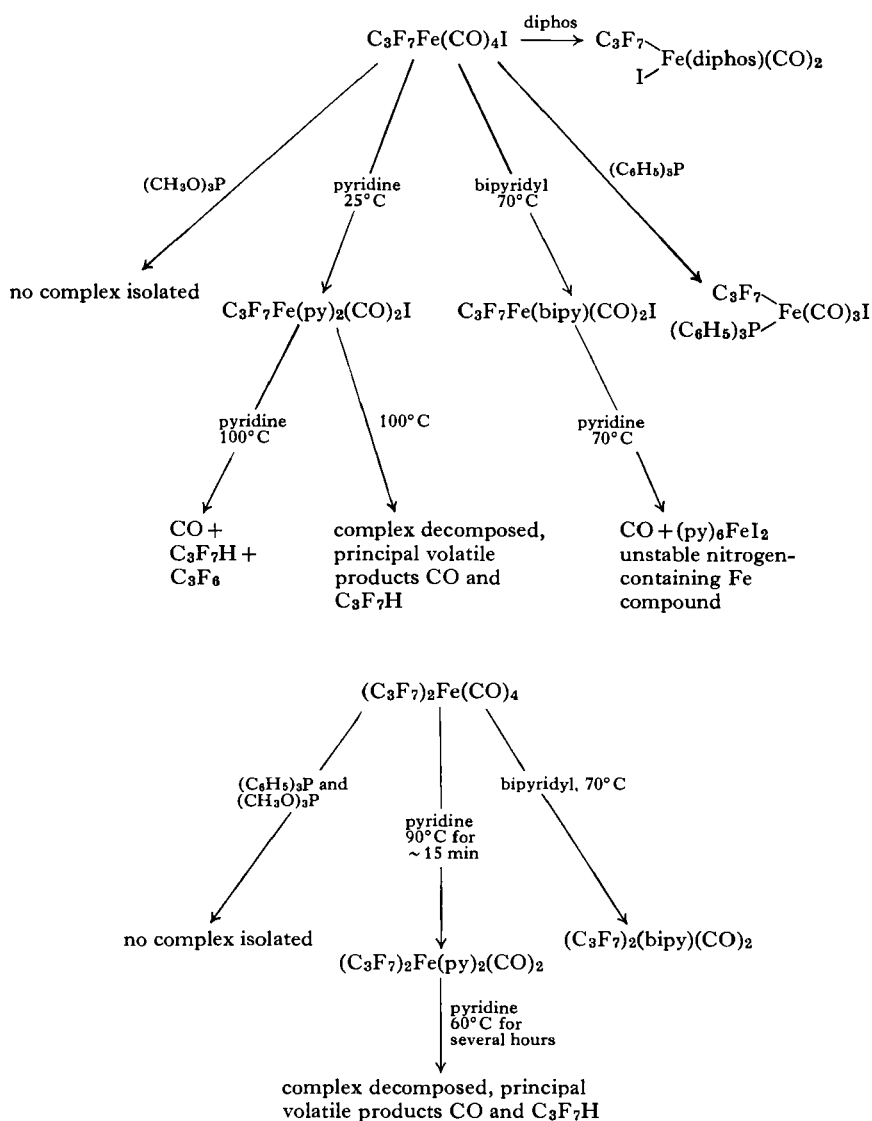
Some studies have been carried out on the replacement by other ligands of carbonyl groups in fluorocarbon derivatives of the metal carbonyls. In Table VI some results obtained using the compounds perfluoro-*n*-propyl-iron tetracarbonyl iodide and bis(perfluoro-*n*-propyl)iron tetracarbonyl are summarized (125, 126). Other substitution reactions of this kind include isolation of the complex $(\text{CF}_2)_4\text{Fe}(\text{CO})_2[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]$ from the reaction between $(\text{CF}_2)_4\text{Fe}(\text{CO})_4$ and the diphosphine (126), and isolation of the complexes $\text{C}_2\text{F}_5\text{Co}(\text{CO})_3[(\text{C}_6\text{H}_5)_3\text{M}]$, M = P, As, or Sb, by

treating perfluoroethylcobalt tetracarbonyl with the appropriate ligand (101). In the case of the complex $\text{C}_2\text{F}_5\text{Co}(\text{CO})_3[(\text{C}_6\text{H}_5)_3\text{P}]$ this compound has also been obtained by treating the salt $\text{NaCo}(\text{CO})_3[(\text{C}_6\text{H}_5)_3\text{P}]$ with the perfluoroacyl halide, as mentioned earlier. Reaction between perfluoroethylcobalt tetracarbonyl and triphenylphosphine with displacement of carbon monoxide is interesting in view of the fact that alkylcobalt tetracarbonyls react *without* loss of carbon monoxide to form acylcobalt–triphenylphosphine tricarbonyls (127, 129). Moreover, methylmanganese pentacarbonyl reacts with carbon monoxide to give acetylmanganese pentacarbonyl (93) but perfluoromethylmanganese pentacarbonyl does not react with carbon monoxide to give trifluoroacetylmanganese pentacarbonyl (94). Evidently the facile transformations between acyl and alkyl metal carbonyls do not occur with the fluoro analogs.

The compound $\text{C}_2\text{F}_5\text{Co}(\text{CO})_3[(\text{C}_6\text{H}_5)_3\text{P}]$ reacts with nitric oxide to give $\text{C}_2\text{F}_5\text{Co}(\text{NO})_2[(\text{C}_6\text{H}_5)_3\text{P}]$ (101). Another nitrosyl compound, $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3\text{-NO}$, has been observed as a product of the reaction between perfluoro-*n*-propyliron tetracarbonyl iodide and sodium nitrite in tetrahydrofuran (123).

These substitution reactions together with those outlined in Table VI suggest that it should be possible to prepare many new compounds starting from fluoroalkyl metal carbonyls. However, the results summarized in Table VI indicate that it might not be possible to replace all the carbonyl groups in the perfluoropropyliron complex by other ligands and still retain a fluorocarbon–metal σ bond. Destruction of fluorocarbon–metal groups by treatment of a complex with certain ligands or with an excess of others could be due to several factors. Many ligands are less effective than carbonyl groups in removing electron density from transition metals by π bonding. Consequently, these ligands would be less able to stabilize any carbon–metal σ bonds which are present in the complex by increasing the energy difference between the highest energy filled orbitals and the lowest energy empty orbital (87, 88), as discussed above in Section VI, A. This could explain why no more than two carbonyl groups in perfluoropropyliron carbonyls can be replaced by pyridine without rupture of the $\text{C}_3\text{F}_7\text{—Fe}$ links (Table VI). Alternatively steric effects may be important. It has been pointed out (126) that steric requirements might explain the failure to isolate the compound *n*- $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{I}$ (125), especially since *n*- $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_2\text{-}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]\text{I}$ has been obtained (126). However, even though the steric requirements of 1,2-bis(diphenylphosphino)ethane may be less than those of two triphenylphosphine molecules, the chelate ligand

TABLE VI

SUBSTITUTION REACTIONS OF $n\text{-C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}$ AND $(n\text{-C}_3\text{F}_7)_2\text{Fe}(\text{CO})_4^a$ ^a The ligand *diphos* is 1,2-bis(diphenylphosphino)ethane.

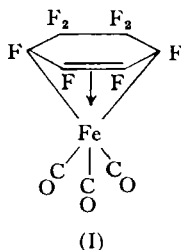
would have a larger ligand field strength which would affect the energy difference between the d levels of iron to a different and unknown degree.

Finally, in discussing the properties of the σ -bonded fluorocarbon-transition metal compounds it is worth noting that those so far reported are all diamagnetic. That this should be so for the majority of the substances is obvious since for the metals the effective atomic number rule is obeyed. However, in the complexes $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Ni(R_F)I$ nickel must be in oxidation state +2 with a d^8 electron configuration. The diamagnetism of these complexes implies a square planar arrangement of the ligands around the nickel atoms.

C. Fluorocarbon π Complexes

The chemistry of hydrocarbon π complexes of the metals has been extensively developed, particularly since the discovery of ferrocene. Preparation of π complexes involving unsaturated fluorocarbons is a logical extension of this work. The report (130) that the product of the reaction between tetrafluoroethylene and iron pentacarbonyl was the olefin complex $(\pi-C_2F_4)_2Fe(CO)_3$ seemed to indicate that many other fluoroolefin-metal complexes would be quickly discovered. However, as discussed in Section VI, B, the iron compound was in fact the heterocyclic iron (+2) tetracarbonyl derivative $(CF_2)_4Fe(CO)_4$ (92, 109, 112). The idea (130) that fluoroethylenes could be π -complexed to metals originated from the modern concept of the nature of bonds between olefins and transition metals. These bonds, sometimes called μ bonds, are believed to be multiple in character, as mentioned previously. A σ linkage involving donation of the π electrons of the olefin to a vacant metal orbital is supplemented by a π bond between d electrons of the metal and vacant π^* antibonding orbitals of the olefin. With fluoroolefins the σ -donor linkage is likely to be very weak due to the inductive effect of the fluorine atoms, but the π bond might be stronger because the fluorine atoms would lower the energy of the π^* orbitals, making them more accessible for bonding (130). It is thus conceivable that under the right conditions a fluoroethylene might be made to complex with a metal, but the concept put forward to account for this possibility was premature in view of the true nature of the compound from tetrafluoroethylene and iron carbonyl. The two dienes 1,3- or 1,4-perfluorocyclohexadiene react with triiron dodecacarbonyl at 120° C to give an air-stable compound of molecular formula $C_6F_8Fe(CO)_3$, m.p. 45° C. Solutions of this compound

in organic solvents slowly decompose in air (112). Spectroscopic studies show that in $C_6F_8Fe(CO)_3$ a 1,3-perfluorocyclohexadiene unit is bonded to an iron tricarbonyl group. Numerous diene-iron tricarbonyl complexes are now known (131, 132) and in view of some recent X-ray crystallographic work (133) it appears that in these complexes the diene may be bound by two σ bonds and a μ bond to three adjacent coordination positions of the iron atom.¹⁹ On this basis $\pi-C_6F_8Fe(CO)_3$ is probably best represented by (I).



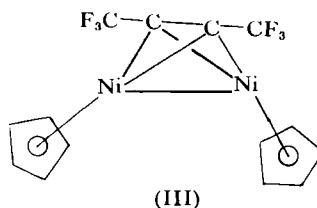
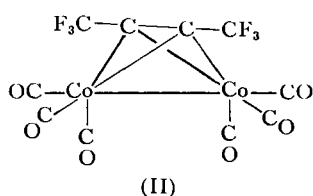
This compound reacts with cesium fluoride in tetrahydrofuran, or dimethylformamide, at room temperature to give $Cs[C_6F_9Fe(CO)_3]$, from aqueous solutions of which the tetramethylammonium salt $(CH_3)_4N[\pi-C_6F_9Fe(CO)_3]$ can be precipitated (134). Many hydrocarbon-metal complexes are now known in which allylic groups are bound to metals by π electrons (132). The anion π -nonafluorocyclohexenyl tricarbonyl ferrate is the first example of a perfluoro- π -allylic metal complex.

Recently several compounds have been described in which transition metals are bonded to carbon atoms which are in turn joined to a CF_3 group. These substances are obtained from reactions between the acetylene hexafluorobut-2-yne and certain metal carbonyls and related compounds. They are obviously closely related to the other fluorocarbon-metal compounds described earlier.

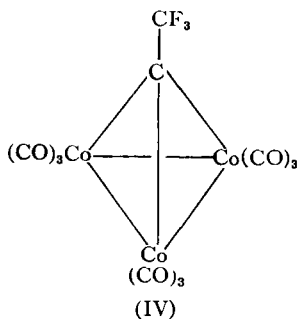
Dicobalt octacarbonyl and π -cyclopentadienylnickel carbonyl react with hexafluorobut-2-yne to give compounds which have been assigned structures (II) and (III) (135, 136). These compounds are stable to air both in the solid state, and as solutions in common organic solvents. They are very volatile. The blood-red cobalt compound [(II), m.p. $114^\circ C$] is stable to

¹⁹ The mode of bonding of dienes to iron or other transition metal atoms is still not completely resolved (see the contribution by Pettit in this volume). Whether the dienes bond to the metals via two σ bonds and a μ bond or via a "sandwich-type" bond of the kind envisaged for the iron-cyclopentadienyl linkages in ferrocene may depend on the electro-negativity of substituents on the diene.

dilute acids and bases. The dark green nickel compound [(III), m.p. 91°C] is attacked by concentrated acids and bases. Compounds similar to (II) and (III) had previously been obtained from several nonfluorine-containing acetylenes and the two carbonyls (137–140). In the case of the cobalt complex $[\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]\text{Co}_2(\text{CO})_6$ the structure, which is like that proposed for



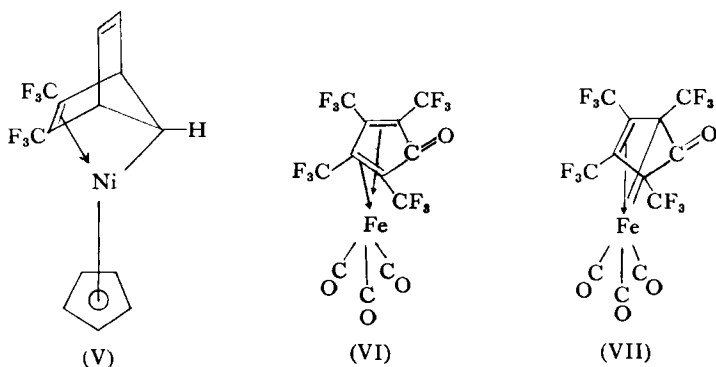
(II), has been firmly established by X-ray crystallography (138). In simple terms the perfluorobut-2-yne unit in (II) and in (III) can be regarded as forming two μ bonds, one to each metal atom. These two bonds, as well as the metal-metal bonds, and the bonds from the carbonyl groups or cyclopentadienyl rings would give each metal atom the krypton electron configuration. In accord with this (II) and (III) are diamagnetic. However, the



bonding of the carbon atoms of the butyne to the cobalt and the nickel atoms in (II) and (III) would undoubtedly be best described in molecular orbital terms, since the butyne may have changed its configuration considerably as has diphenyl acetylene in $[\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]\text{Co}_2(\text{CO})_6$ (138), and the metal-metal bonds would be bent like the Co-Co bonds in $\text{Co}_2(\text{CO})_8$. A molecular orbital description would probably also best account for the bonding in the novel compound $\text{F}_3\text{CC}[\text{Co}(\text{CO})_3]_3$ obtained by treating cobalt carbonyl with $\text{CF}_3\text{CBr}_2\text{Cl}$ in ethanol, and assigned structure (IV). A similar compound $\text{FC}[\text{Co}(\text{CO})_3]_3$ was obtained from trichlorofluoromethane and cobalt

carbonyl (140a). These substances are probably best regarded as intermediate in bond character between the σ -bonded fluorocarbon metal derivatives of Section VI, B and the fluorocarbon π complexes reviewed in this section.

Compound (III) is also formed in the reaction between di- π -cyclopentadienylnickel (nickelocene) and perfluorobut-2-yne (102a, 123). However, the novel compound (V) is also produced in about equal quantity. Complex (V) is an orange diamagnetic solid (m.p. 74° C). A similar compound with a μ and a σ bond from carbon atoms to nickel had previously been obtained



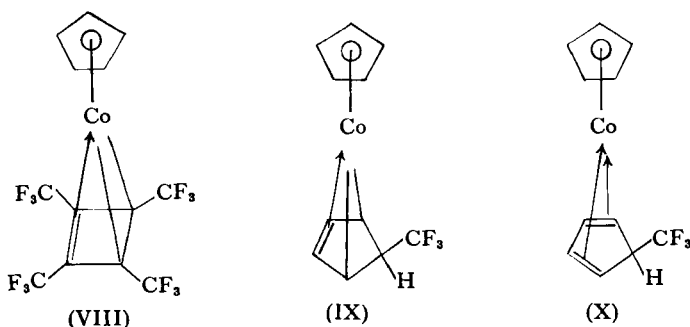
from the reaction between nickelocene and dimethyl acetylenedicarboxylate (141).

As with nickelocene, perfluorobut-2-yne reacts with iron pentacarbonyl and π -cyclopentadienylcobalt dicarbonyl to form complexes in which the acetylene group is no longer evident (136). From iron pentacarbonyl a volatile orange-yellow compound C₉F₁₂OFe(CO)₃ (m.p. 157° C) is obtained. Its solutions in air decompose very slowly, and the compound is decomposed by bases. However, it dissolves in concentrated sulfuric acid to form an orange solution from which it can be recovered. The spectroscopic (NMR and infrared) properties of the iron compound are in accord with a structure in which a tetrakis(trifluoromethyl)cyclopentadienone ring is bound to an iron tricarbonyl group. Bonding of the ring to the iron could occur by means of two μ bonds (VI) or by means of one μ bond and two σ bonds (VII) (136). In view of the recent X-ray crystallographic studies (133) on diene-iron tricarbonyl complexes, structure (VII) seems more likely.²⁰ It should be noted that several cyclopentadienone-metal carbonyl complexes derived from

²⁰ But see previous footnote.

nonfluorinated acetylenes have been described during the last decade (131, 133). The ketone group in (VII) does not react with 2,4-dinitrophenylhydrazine or semicarbazide. This deactivation, however, is not surprising in view of a similar inactivity shown by tetraphenylcyclopentadienone-iron tricarbonyl (142). Complex (VII) reacts with triphenylphosphine with displacement of carbon monoxide to form $C_9F_{12}OFe(CO)_2P(C_6H_5)_3$.

π -Cyclopentadienylcobalt dicarbonyl reacts with perfluorobut-2-yne to give a red, air-stable compound, $\pi-C_5H_5CoC_8F_{12}$, m.p. $166^\circ C$. This substance is extremely stable chemically, and can be recovered after treatment with butyllithium, concentrated nitric acid, bromine, and several other reagents (136). On the basis of its diamagnetism and infrared and NMR



spectroscopic properties the structure proposed (136) for $\pi-C_5H_5CoC_8F_{12}$ is (VIII), in which the cobalt atom is formally in a +3 oxidation state. The carbonyls $Fe(CO)_5$ and $\pi-C_5H_5Co(CO)_2$ give similar products with many reagents. It is, therefore, very surprising that π -cyclopentadienylcobalt dicarbonyl reacts with perfluorobut-2-yne to give (VIII) rather than a tetrakis(perfluoromethyl)cyclopentadienone complex analogous to (VII).²¹

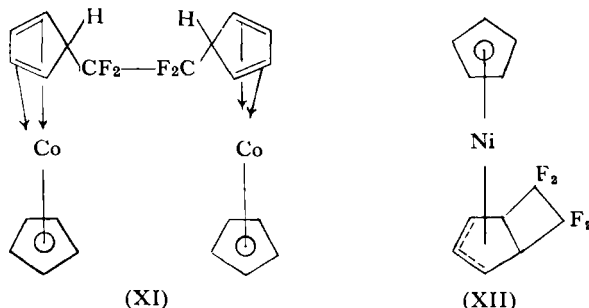
The blood-red liquid obtained by treating cobaltocene with perfluoromethyl iodide (112) could be formulated as (IX) with the cobalt atom formally in a +3 oxidation state, rather than (X) with two μ bonds, but an X-ray study would be required to settle this point, as well as whether the CF_3 group is in the *endo* or *exo* position.

In concluding this survey of fluorocarbon π complexes of transition metals it is of interest to mention two compounds which, although they do not have

²¹ Recent X-ray crystallographic studies, reported (142a) since this chapter was written, have indeed shown that (VIII) described in reference (136) as having the formula " $\pi-C_5H_5CoC_8F_{12}$ " contains the tetrakis(perfluoromethyl)cyclopentadienone group, and the structure is in fact similar to that of (VII).

fluorocarbon groups π -complexed to metals, are derived from tetrafluoroethylene.

Cobaltocene and tetrafluoroethylene afford a red-brown diamagnetic air-stable compound which decomposes at 140°C . For this compound spectroscopic studies strongly suggest structure (XI), in which two cyclopentadiene rings are joined in the *endo* positions by $-\text{CF}_2\text{CF}_2-$ (112).



Nickelocene and tetrafluoroethylene in tetrahydrofuran at 80°C yield air-stable, volatile, red crystals, m.p. 93°C (143). NMR (143) and other studies (123) establish the structure of this complex as (XII). The compound belongs to a family of recently characterized π -allylnickel complexes (132). A similar compound is formed by chlorotrifluoroethylene and nickelocene (143).

VII

DERIVATIVES OF GROUP IIB ELEMENTS

A. Zinc and Cadmium

Few fluorocarbon derivatives of these two elements have been characterized. Early attempts to prepare organozinc compounds from trifluoromethyl iodide or pentafluoroethyl iodide and zinc afforded only fluoroform or pentafluoroethane (6). Subsequently, perfluoro-*n*-propylzinc iodide was prepared in about 75% yield by treating zinc dust with heptafluoro-*n*-propyl iodide using dioxane or aliphatic ethers as solvents (144, 145). As in the case of the Grignard reagents, $\text{R}_\text{F}\text{MgI}$ (Section III), the yield of organometallic is very dependent on the reaction temperature, with maximum yield near 0°C . Concentration of reagents is also important, with dilution favoring

higher yields. During formation of the perfluoro-*n*-propylzinc compound small amounts of heptafluoropropane and hexafluoropropene were also produced. As mentioned previously (Section II), these could arise by decomposition of the anion $C_3F_7^-$ either by release of fluoride ion to form hexafluoropropene or by attack on the solvent to give heptafluoropropane. However, ether solutions of perfluoro-*n*-propylzinc iodide are stable for prolonged periods at room temperature. This thermal stability in solution is in striking contrast to that of *n*- C_3F_7Li or *n*- C_3F_7MgI , and suggests that the heptafluoropropane forms by free radical abstraction of a hydrogen atom from solvent rather than by removal of a proton by the $C_3F_7^-$ carbanion (145).

Perfluoro-*n*-propylzinc iodide was characterized by the release of heptafluoropropane on addition of aqueous reagents, and by reaction with acetyl chloride to give the ketone, $CH_3COC_3F_7$. Perfluoro-*n*-propylzinc iodide however, does not react with carbon dioxide, and in general, appears to be less reactive than perfluoro-*n*-propylmagnesium iodide.

From the reaction between zinc dust and heptafluoro-*n*-propyl iodide in dioxane it is possible to obtain, after evaporation of the solvent, the pale yellow solid $C_3F_7Zn(\overline{CH_2OCH_2CH_2OCH_2})I$. High vacuum sublimation removed the dioxane to give colorless perfluoro-*n*-propylzinc iodide (144). The latter, on heating to $180^\circ C$ produced hexafluoropropene and a mixture of zinc fluoride and zinc iodide. It is interesting to compare this reaction with the effect of heat on alkylzinc iodides, which affords dialkylzinc compounds. Solutions of perfluoro-*n*-propylzinc iodide do not react with air, in striking contrast to substances containing alkyl-zinc bonds.

Perfluoroalkylcadmium compounds have received only brief mention in the chemical literature (3, 146).

B. Mercury

As mentioned in the Introduction, the first fluorocarbon-metal compounds to be discovered were derivatives of mercury (1-5). Since they (Table VII) were the subject of a recent review (5) a less thorough treatment will be given here, with the exception of those compounds reported since 1960.

Perfluoroalkylmercury iodides are obtained either by irradiating with ultraviolet light, or by heating, mixtures of perfluoroalkyl iodides and mercury. The iodides, R_FHgI , are white, crystalline, water-soluble solids when

$R_F = CF_3$ or C_2F_5 , but the compound $n-C_3F_7HgI$ is not appreciably soluble. The perfluoroalkyl groups can be removed by hydrolysis, but the compounds CF_3HgX ($X = F, Cl, Br$ and NO_3) have been prepared by treating perfluoromethylmercury iodide with moist silver oxide followed by the appropriate aqueous acid.

TABLE VII
PHYSICAL PROPERTIES OF POLYFLUOROALKYL DERIVATIVES OF MERCURY^a

Compound	M.p. (°C, sealed tube)	Compound	M.p. (°C, sealed tube)
$(CF_3)_2Hg$	163	C_2F_5HgI	98 ^b
CF_3HgCl	76	C_2F_5HgOH	220–225
CF_3HgBr	83	$(CF_3CH_2)_2Hg$	40
CF_3HgI	112.5 ^b	$(CF_3CHF)_2Hg$	78–79
CF_3HgOH	130/10 ⁻⁵ mm ^c	$(CF_3CFCI)_2Hg^d$	93–95
CF_3HgNO_3	100/10 ⁻⁵ mm ^c	$CF_3CFCIHgF$	118
$(C_2F_5)_2Hg$	106–107	C_3F_7HgI	77.0–77.5 ^b
C_2F_5HgF	99–100	$[(CF_3)_2CF]_2Hg$	20–21 ^e
C_2F_5HgCl	103–104	$[(CF_3)_3C]_2Hg$	65–66
C_2F_5HgBr	78–79	$[HCF_2CF_2C(CF_3)F]_2Hg$	173

^a This table is largely a reproduction of a table given in ref. (5).

^b These melting points are affected appreciably, while remaining sharp, by traces of mercury iodides formed during purification or on storage. This renders the values quoted somewhat uncertain.

^c Sublimation temperature.

^d Not pure.

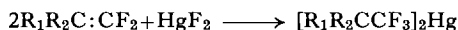
^e B.p. 116–117°.

Standard methods which convert alkylmercury iodides into bis(alkyl)mercurials fail to convert perfluoroalkylmercury iodides into bis(perfluoroalkyl)mercurials. The preparation of primary bis(perfluoroalkyl)mercurials can be accomplished by treating perfluoroalkylmercury iodides with silver, copper, or cadmium amalgams. Alternatively, the parent perfluoroalkyl iodide will react directly with the amalgam. By either method yields are from 40 to 90%.

A convenient new synthesis of bis(polyfluoroethyl)mercurials, involving addition of mercury(II) fluoride to fluoroethylenes, under autogenous pressures at 50–100° C, has recently been described (147). In this manner

the compounds $(C_2F_5)_2Hg$, $(CF_3CHF)_2Hg$, and $(CF_3CH_2)_2Hg$ have been obtained in yields of about 60%. It is necessary to use a solvent, preferably arsenic trifluoride, for these addition reactions. The structure of the products from trifluoroethylene and 1,1-difluoroethylene, together with the necessity for a polar solvent for reaction, is in accord with an ionic mechanism for the additions. Mercury(II) fluoride also adds to the double bond of chlorotrifluoroethylene at 100° C in the absence of a solvent, giving the mercurial $CF_3CFCIHgF$ (148). The structure of this compound was established by cleavage of the organic group with aqueous sodium stannite to give CF_3CHFCl , and with chlorine to give CF_3CFCl_2 . In the presence of arsenic trifluoride, mercury(II) fluoride and chlorotrifluoroethylene afford $(CF_3CFCI)_2Hg$, but this compound was not obtained pure (147).

Addition of mercury(II) fluoride to terminally unsaturated fluoroolefins affords branched fluoroalkyl mercurials. Until recently no routes to such compounds were known (148a).



Reaction proceeds readily with a large number of fluoroolefins when anhydrous hydrogen fluoride is used as a solvent, with temperatures in the range 100–150° C, under autogenous pressure. In this manner the compounds $[(CF_3)_2CF]_2Hg$, $[HCF_2CF_2C(CF_3)F]_2Hg$, $[ClCF_2CF_2C(CF_3)F]_2Hg$, $[H(CF_2)_8(CF_3)CF]_2Hg$, and $[(CF_3)_3C]_2Hg$ were obtained, their structures being established by F^{19} NMR studies.

Bis(trifluoromethyl)mercury, a crystalline solid with an irritating odor, is soluble in organic solvents and can be sublimed readily (149). Above 160° C it decomposes. This is approximately 150° C below the temperature at which appreciable thermal decomposition of dimethylmercury occurs. Bis(perfluoroalkyl)mercurials decompose in the presence of ultraviolet light to give R_F radicals, which will initiate the polymerization of olefins. Halogens convert bis(perfluoroalkyl)mercurials into mercury(II) halides and the expected R_FX compound. Several reagents in aqueous media react with the bis(perfluoroalkyl)mercurials to cleave the fluorocarbon group as the monohydroperfluoroalkane, R_FH . In this respect mercury behaves more like tin or lead than like the transition metals. Perfluoroalkyl derivatives of the latter afford mainly fluoride ion on decomposition under aqueous conditions, whereas perfluoroalkyltin and -lead compounds yield R_FH quantitatively under these conditions.

Unlike alkylmercurials, which transfer their alkyl groups to other metals

or which will alkylate certain metal halides, perfluoroalkylmercurials do not function at all readily as perfluoroalkylating reagents. Apparently the pseudohalogen character of perfluoroalkyl groups renders the perfluoroalkylmercurials more similar in properties to mercury(II) halides than organomercurials. Related to this is the solubility of bis(trifluoromethyl)-mercury in water, but the aqueous solutions give no indication of the presence of Hg^{2+} ions and the compound can be recovered unchanged (89). It is especially significant that aqueous solutions of $(\text{CF}_3)_2\text{Hg}$, CF_3HgI , or $\text{C}_3\text{F}_7\text{HgI}$ can be conductometrically titrated with potassium halides, thereby revealing the formation of complex anions $[(\text{CF}_3)_2\text{HgX}_2]^{2-}$, $[\text{R}_\text{F}\text{HgIX}]^-$, and $[\text{R}_\text{F}\text{HgIX}_2]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{R}_\text{F} = \text{CF}_3, n\text{-C}_3\text{F}_7$) (150). The complex anions decrease in stability in passing from the iodo to the chloro ions. The perfluoroalkylhalogenmercurate(II) anions are related to the well-known tetrahalogenomercurate(II) ions such as $[\text{HgI}_4]^{2-}$.

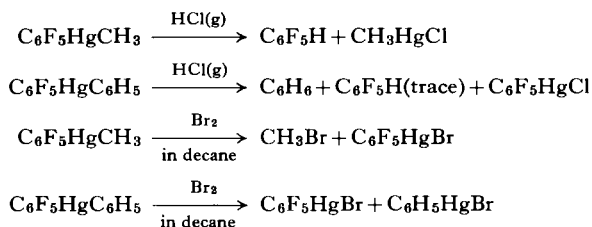
Solutions containing the ions $[\text{CF}_3\text{HgI}_3]^{2-}$, $[\text{C}_3\text{F}_7\text{HgI}_3]^{2-}$, and $[(\text{CF}_3)_2\text{HgI}_2]^{2-}$ react with ethylenediamine-transition metal complexes with precipitation of compounds like $[\text{en}_3\text{Ni}][(\text{CF}_3)_2\text{HgI}_2]$, $[(\text{en})_3\text{Zn}][\text{C}_3\text{F}_7\text{HgI}_3]$, and $[(\text{en})_2\text{Cu}][\text{CF}_3\text{HgI}_3]$ (150). These complexes closely resemble the corresponding compounds containing HgX_4^{2-} anions. Complex compounds of the type $(\text{R}_\text{F})_2\text{HgL}$ and $(\text{R}_\text{F})_2\text{HgL}_2$ ($\text{L} = \text{piperidine, pyridine, triphenylphosphine, triphenylarsine, pyridine } N\text{-oxide, etc.}$) have been shown by oscillometric titration to exist in benzene solution (150a).

The field of fluorocarbon-mercury compounds has recently been expanded by the isolation of the pentafluorophenylmercurials $(\text{C}_6\text{F}_5)_2\text{Hg}$, (m.p. 142.3°C), $\text{C}_6\text{F}_5\text{HgCH}_3$ (m.p. 36°C), $\text{C}_6\text{F}_5\text{HgC}_6\text{H}_5$ (m.p. 164°C) and $\text{C}_6\text{F}_5\text{HgBr}$ (m.p. 155°C) (151).

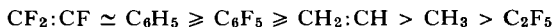
Pentafluorophenylmagnesium bromide reacts readily with mercury(II) chloride to give bis(pentafluorophenyl)mercury, which may be recrystallized from carbon tetrachloride as white crystals. The thermal stability of the mercurial is high; a sample heated at 250°C for 5 hours *in vacuo* was unaffected. Apparently fluorine migration from the pentafluorophenyl group to mercury, thereby affording tetrafluorobenzene, does not occur readily. Bis(pentafluorophenyl)mercury resists decomposition by protonic acids. It may be recrystallized from concentrated sulfuric acid. In carbon tetrachloride equimolar quantities of bromine and bis(pentafluorophenyl)-mercury at 60°C yield pentafluorophenylmercuric bromide and pentafluorobromobenzene. Bis(pentafluorophenyl)mercury is unusual in its ability to react with bipyridyl and with 1,2-bis(diphenylphosphino)ethane to form

the complexes, $(\text{C}_6\text{F}_5)_2\text{Hg}(\text{bipy})$ and $(\text{C}_6\text{F}_5)_2\text{Hg}(\text{diphos})$, with melting points of 122°C and 158°C , respectively. Analogous complexes are not formed by diarylmercurials.

The compound methylpentafluorophenylmercury has been obtained by adding an ether suspension of methylmercury(II) iodide to pentafluorophenylmagnesium bromide in ether. In the same manner, pentafluorophenylphenylmercury has been obtained from phenylmercury(II) chloride. The following cleavage reactions have been observed:



The products of the hydrogen chloride cleavage reactions indicate that the position of the C_6F_5 group in the organometal cleavage series (see Section V, C) is,



The nature of the products from the bromine cleavage reactions was unexpected, since groups removed by bromine from organomercurials, organotin, or related organometallic compounds are normally the same as those removed by hydrogen chloride. Formation of methyl bromide, and approximately equal amounts of phenylmercury(II) bromide and pentafluorophenylmercury(II) bromide in the two reactions suggests that different mechanisms must operate for the reactions with bromine and hydrogen chloride. The ability of the pentafluorophenyl group to influence the acceptor properties of mercury to a considerable degree, as evidenced by the dipyriddy and diphosphine complexes mentioned above, has led to the suggestion (151) that the reactions with bromine involve an intermediate in which molecular bromine is coordinated to mercury. Factors determining the decomposition of such an intermediate could well be different from those which determine the course of electrophilic attack by hydrogen chloride.

Mixtures of bis(pentafluorophenyl)- and dimethylmercury equilibrate to give methylpentafluorophenylmercury. However, this exchange occurs only in the presence of halide promoters, e.g. pentafluorophenylmercury(II) bromide.

VIII

SPECTROSCOPIC STUDIES

Both infrared spectroscopy and nuclear magnetic resonance spectroscopy have played an important part in advancing our knowledge of fluorocarbon-metal compounds. Indeed, without the use of these spectroscopic techniques, elucidation of the structures of many of the compounds described in the preceding sections would have been long delayed.

A. Nuclear Magnetic Resonance Spectroscopy

The F^{19} nucleus is almost as suitable as the proton for NMR work and the large fluorine chemical shifts minimize second order effects, thereby permitting meaningful deductions to be made about molecular structure. The F^{19} spectra of many of the recently described fluorocarbon-metal derivatives have been recorded, and the chemical shifts and spin coupling constants listed. References to these studies are collected in Table VIII.

Since they illustrate an important point, the F^{19} spectra of the compounds $n-C_3F_7Sn(n-C_4H_9)_3$, $n-C_3F_7CRe(CO)_5$, and $n-C_3F_7Re(CO)_5$ are reproduced in Fig. 1. It will be seen that a large shift to low field is found for the absorption by a CF_2 group bonded directly to a transition metal (153). This absorption is generally centered from about 55 to 73 ppm, relative to CCl_3F (0.0 ppm), increasing to high field. However, shifts somewhat outside this range have been observed; for example, $\delta(\alpha-CF_2)$ in $HCFCICF_2-Mn(CO)_5$ and $C_2F_5Re(CO)_5$ occur at 53.1 ppm and at 74.9 ppm, respectively. This unshielding effect is a useful diagnostic test for the presence of the group $-CF_2-M$, where M is a transition metal. It helped to establish, for example, that the product of the reaction, carried out at 5–10 atm pressure, between manganese pentacarbonyl hydride and 1,1-dichloro-2,2-difluoroethylene contained the group $HCCl_2CF_2Mn$ rather than HCF_2CCl_2Mn (97). The absorption appears as a doublet (splitting 10.5 cps) at 45.8 ppm. The low position of the fluorine resonance and the small J_{FH} value support the $HCCl_2CF_2Mn$ structure. With perfluoroalkyl derivatives of main group metals no large shift to low field of the resonance of the $\alpha-CF_2$ groups is observed (153)²²

²² It has recently been observed (153a) that the F^{19} shifts of the *ortho* fluorine atoms in pentafluorophenyl transition metal complexes are less shielded than similar fluorine atoms in pentafluorophenyl derivatives of main group metals. For possible reasons for the relative shifts in $-CF_2-M$ and C_6F_5-M compounds, see refs. (153) and (153a).

TABLE VIII
F¹⁹ NUCLEAR MAGNETIC RESONANCE STUDIES

Compound	Reference	Compound	Reference
<i>Sigma-bonded fluoroorganic groups</i>			
<i>Boron</i>			
CF ₂ :CFBCl ₂	(56)	(CF ₂ :CF) ₃ B	(56)
CF ₂ :CFBF ₂	(56)	[CF ₃ BF ₃] ⁻	(152)
<i>Silicon</i>			
(CF ₂ :CF) ₂ Si(C ₂ H ₅) ₂	(56)	(C ₆ H ₅) ₃ GeCF:CFSi(C ₂ H ₅) ₃	(60)
CF ₂ :CFSi(C ₂ H ₅) ₃	(68)	C ₃ H ₇ SCF:CFSi(C ₂ H ₅) ₃	(60)
CF ₂ :CFSi(OC ₂ H ₅) ₃	(68)	C ₆ H ₅ SCF:CFSi(C ₂ H ₅) ₃	(60)
C ₄ H ₉ CF:CFSi(C ₂ H ₅) ₃	(60)	C ₆ H ₅ CF:CFSi(C ₂ H ₅) ₃	(60)
CH ₂ :CHCH ₂ CF:CFSi(C ₂ H ₅) ₃	(60)	C ₂ H ₅ OCF:CFSi(C ₂ H ₅) ₃	(60)
(C ₆ H ₅) ₃ SiCF:CFSi(C ₂ H ₅) ₃	(60)	(CH ₃) ₃ SiCH ₂ OCF:CFSi(C ₂ H ₅) ₃	(60)
<i>Germanium</i>			
CF ₂ :CFGe(C ₂ H ₅) ₃	(68)	(CF ₂ :CF) ₄ Ge	(56)
(CF ₂ :CF) ₂ Ge(CH ₃) ₂	(56)		
<i>Tin</i>			
(CF ₂ :CF) ₂ Sn(CH ₃) ₂	(56)	CF ₂ :CFSn(C ₂ H ₅) ₃	(68)
CF ₂ :CFSn(<i>n</i> -C ₄ H ₉) ₃	(56)	(CF ₂ :CF) ₂ Sn(C ₆ H ₅) ₂	(56)
(C ₂ F ₅) ₂ Sn(CH ₃) ₂	(153)	C ₂ F ₅ Sn(<i>n</i> -C ₄ H ₉) ₃	(153)
C ₂ F ₅ Sn(C ₂ H ₅) ₃	(153)	<i>n</i> -C ₃ F ₇ Sn(<i>n</i> -C ₄ H ₉) ₃	(153)
CF ₃ Sn(CH ₃) ₃	(154)	CF ₃ Sn(CH ₃) ₂ Cl	(154)
<i>Group V</i>			
(<i>n</i> -C ₃ F ₇) ₂ PI	(153)	(CF ₂ :CF) ₃ As	(56)
(<i>n</i> -C ₃ F ₇) ₂ PCl	(153)		
<i>Mercury</i>			
(CF ₂ :CF) ₂ Hg	(56)	(CF ₃ CHF) ₂ Hg	(147)
(CF ₃ CH ₂) ₂ Hg	(147)	[(CF ₃) ₂ CF] ₂ Hg	(148a)
<i>Transition metals</i>			
π-C ₅ H ₅ Mo(CO) ₃ CF ₂ CF ₂ H	(113)	π-C ₅ H ₅ W(CO) ₃ CF ₂ CF ₂ H	(113)
CF ₃ Mn(CO) ₅	(95)	C ₂ F ₅ COMn(CO) ₅	(153)
C ₂ F ₅ Mn(CO) ₅	(153)	HCF ₂ CF ₂ COMn(CO) ₅	(97)
<i>n</i> -C ₃ F ₇ Mn(CO) ₅	(153)	HCFClCF ₂ Mn(CO) ₅	(97)
HCF ₂ CF ₂ Mn(CO) ₅	(97)	CF ₃ CH:C(CF ₃)Mn(CO) ₅	(97)
HCCl ₂ CF ₂ Mn(CO) ₅	(97)	<i>trans</i> -CF ₃ CF:CFMn(CO) ₅	(119)

continued

TABLE VIII (continued)

Compound	Reference	Compound	Reference
$C_2F_5Re(CO)_5$	(153)	$C_2F_5CORe(CO)_5$	(153)
$n-C_3F_7Re(CO)_5$	(153)	$n-C_3F_7CORe(CO)_5$	(153)
$CF_3Fe(CO)_4I$	(153)	$C_2F_5Fe(CO)_4I$	(153)
$(C_2F_5)_2Fe(CO)_4$	(153)	$n-C_3F_7Fe(CO)_4I$	(153)
$(n-C_3F_7)_2Fe(CO)_4$	(153)	$(CF_2)_4Fe(CO)_4$	(92, 112)
$trans-CF_3CF:CFFe$	(119)	$(HCF_2CF_2)_2Fe(CO)_4$	(106)
$(\pi-C_5H_5)(CO)_2$			
$n-C_3F_7Co(\pi-C_5H_5)(CO)I$	(153)	$CF_3Co(CO)_4$	(95)
$C_2F_5Co(CO)_4$	(95)	$n-C_3F_7Co(CO)_4$	(95)
$(CF_2)_4Co(\pi-C_5H_5)(CO)$	(110)	$(CO)_4CoCF_2CF_2Co(CO)_4$	(112)
$CF_3Ni(\pi-C_5H_5)(CO)$	(102a, 123)	$n-C_3F_7Ni(\pi-C_5H_5)(CO)$	(102a, 123)
$C_2F_5Ni(\pi-C_5H_5)(CO)$	(102a, 123)	$C_2F_5Ni(\pi-C_5H_5)[(C_6H_5)_3P]$	(102a, 123)
$C_3F_5Ni(\pi-C_5H_5)(CO)^a$	(102a, 123)	$C_4F_5Ni(\pi-C_5H_5)[(C_6H_5)_3P]^b$	(102a, 123)
<i>Pi-complexed fluoroorganic groups^c</i>			
I, $\pi-C_6F_8Fe(CO)_3$	(112)	VII, $\pi-C_9F_{12}OFe(CO)_3$	(136)
II, $(CF_3C\equiv CCF_3)_2Co_2(CO)_8$	(136)	VIII, $\pi-C_5H_5Co-\pi-C_8F_{12}$	(136)
III, $(CF_3C\equiv CCF_3)Ni_2-$	(136)	XI, $(\pi-C_5H_5Co-\pi-C_5H_5CF_2)_2$	(112)
$(\pi-C_5H_5)_2$			
V, $\pi-C_5H_5Ni-\pi-C_9F_8H_5$	(143)	XII, $\pi-C_5H_5Ni-\pi-C_7H_5F_4$	(123, 143)

^a Prepared as a mixture of $\sigma-CF_2:CFCF_2Ni(\pi-C_5H_5)(CO)$ and $trans-\sigma-CF_3CF:CFNi(\pi-C_5H_5)(CO)$.^b The C_4F_5-Ni group appears to be $\sigma-CF_2:CFCF:CF-Ni$.^c Compounds are referred to by Roman numeral; for proposed molecular structures see pages 196–200. However, VIII is now known to be $\pi-C_5H_5CoC_9F_{12}O$ (142a).

F^{19} NMR studies have been particularly helpful in determining the structures of $(CF_2)_4Co(CO)(\pi-C_5H_5)$, $trans-CF_3CF:CFFe(CO)_2(\pi-C_5H_5)$, and related complexes, and the products obtained by treating triethylperfluorovinylsilane with organolithium reagents.

It has been mentioned previously (Section VI, B) that the complex $(CF_2)_4Fe(CO)_4$ is the product of the reaction between iron pentacarbonyl and tetrafluoroethylene. The symmetrical substitution of the metal atom affords equivalent sets of fluorine atoms above and below the ring. This symmetry is reflected in the 56.4 mc F^{19} spectrum, which shows two sets of

signals corresponding to two pairs of CF_2 groups. Spin coupling between adjacent CF_2 groups is about 2 cps. In the compound $(\text{CF}_2)_4\text{Co}(\text{CO})-(\pi\text{-C}_5\text{H}_5)$, obtained from tetrafluoroethylene and π -cyclopentadienylcobalt dicarbonyl (Section VI, B), the metal atom is asymmetrically substituted. Consequently, fluorine atoms on either side of the $(\text{CF}_2)_4\text{Co}$ ring are nonequivalent, which leads to a 354 cps chemical shift between the

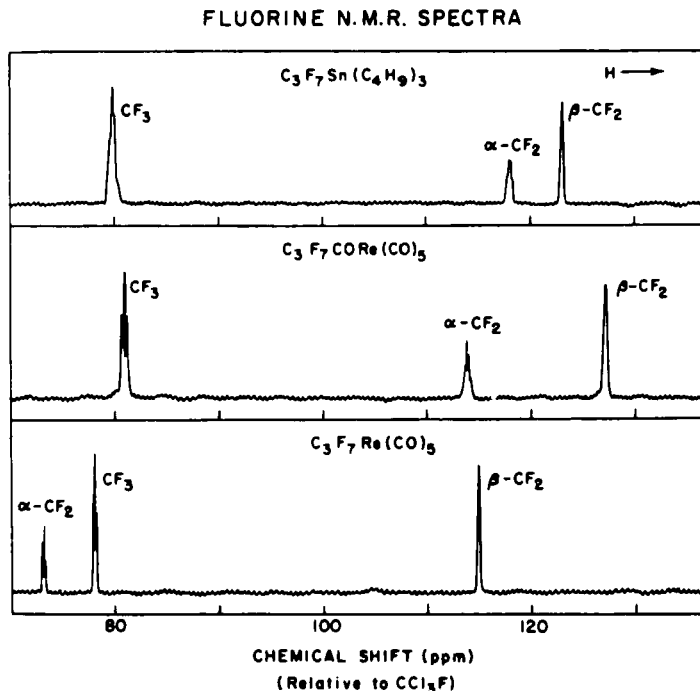


FIG. 1. Fluorine NMR spectra.

fluorine atoms in the $\alpha\text{-CF}_2$ groups (Fig. 2). The nonequivalence of the fluorine atoms in the $\beta\text{-CF}_2$ groups is not as large, but is seen as small satellite signals at 7.35 and 7.85 kc from CCl_3F . The observation of a chemical shift between the fluorine atoms in the CF_2 groups adjacent to the cobalt atom strongly supports the structure proposed for $(\text{CF}_2)_4\text{-Co}(\text{CO})(\pi\text{-C}_5\text{H}_5)$ (110).

A compound $\text{C}_3\text{F}_5\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ is obtained by treating the salt $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ with perfluoroallyl chloride (Section VI, B). The pattern of the F^{19} spectrum of the iron compound consists of *three* multiplets

of relative intensity of 3:1:1 (119). On the basis of simple first order theory the F^{19} NMR spectrum of a perfluoroallyl group would be expected to consist of *four* multiplets with the intensity ratio 2:1:1:1; the strongest multiplet would consist of eight lines of equal intensity and each of the other multiplets would appear as four triplets. Clearly the iron complex does not contain the $CF_2:CF CF_2 Fe$ group. In fact in the 3:1:1 pattern observed, the largest multiplet is a quartet of intensity ratio 1:1:1:1 while each of the

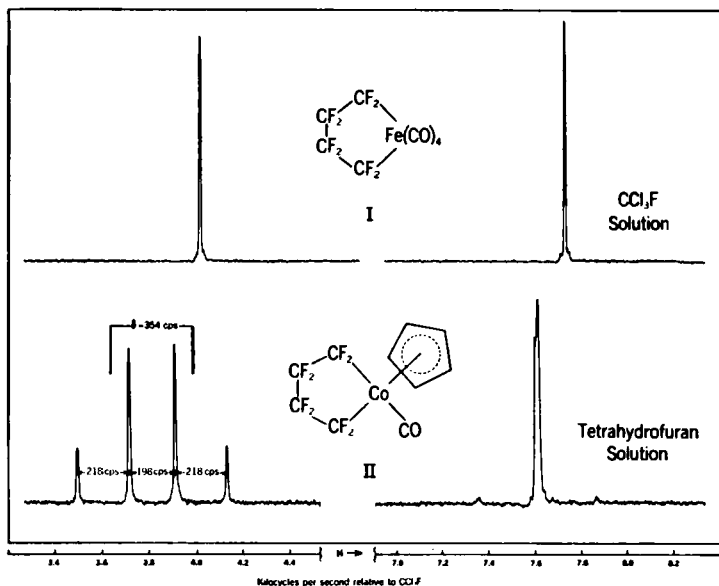
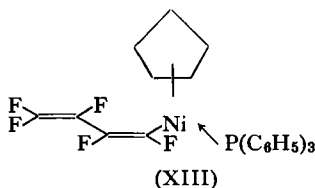


FIG. 2. F^{19} NMR spectra of the heterocyclic compounds obtained by treating iron pentacarbonyl or π -cyclopentadienylcobalt dicarbonyl with tetrafluoroethylene. Spectra taken at 56.4 mc. Reproduced by permission of the Varian Associates' "NMR at Work" Series, No. 81.

two weaker absorptions is a doublet, both lines of each doublet being further split into quartets of intensity ratio 1:3:3:1; this spectrum accords with the presence of a perfluoropropenyl group, $CF_3CF:CF$, bonded to iron. Of further interest is the possible isomeric character of $\sigma-CF_3CF:CFFe(CO)_2-(\pi-C_5H_5)$. The relative simplicity of the F^{19} spectrum indicates that a single isomer is present, predominantly if not exclusively. The observed coupling constant ($J_{FF} = 131$ cps) establishes that the single isomer formed is the *trans* isomer, because in fluoroolefins spin coupling constants J_{FF} (*trans*) are generally of the order of 125 cps, whereas spin coupling constants J_{FF} (*cis*)

are of the order 19–60 cps. Similar arguments have been used to determine the structure of the fluoroorganic group in *trans*-CF₃CF:CFMn(CO)₅ (119). As mentioned previously (Section VI, B), treatment of the salt π -C₅H₅-Ni(CO)K with perfluoroallyl chloride affords a material of composition π -C₅H₅Ni(CO)C₃F₅. The F¹⁹ spectrum of this material is very similar to that shown by a mixture of perfluoroallyl chloride and σ -CF₃CF:-CFMn(CO)₅, showing that both the groups σ -CF₂:CFCF₂Ni and σ -*trans*-CF₃CF:CFNi are present in the nickel compound (102a, 123).

The F¹⁹ nuclear resonance spectra of the compounds (C₂H₅)₃SiCF:CFR [R = C₆H₅, Si(C₆H₅)₃, and Ge(C₆H₅)₃] have been examined in order to determine their isomeric character (60). The observed *J*_{FF} spin coupling constants are 124, 132, and 144 cps, respectively. The large values observed show that the fluorine atoms are in the *trans*-position to each other.



F¹⁹ NMR spectroscopy has also played an important part in establishing the structures of Hg(CHF₂CF₃)₂, Hg(CH₂CF₃)₂ (147), and CF₃CH:C-(CF₃)Mn(CO)₅ (97), as well as indicating the nature of the C₄F₅Ni group in the compound C₄F₅Ni(π -C₅H₅)(C₆H₅)₃P (Section VI, B). The spectrum of the latter consists of five multiplets of equal intensity, each multiplet consisting of sixteen equally intense lines (102a, 123). This is the pattern expected for five spin-coupled nonequivalent fluorine atoms. The three high field resonances display chemical shifts [δ = 153, 107, and 119 ppm, relative to CCl₃F (0.00 ppm) increasing to high field] and coupling constants (*J* = 113, 23, 82 cps), very similar to those observed for the CF₂:CF group in chlorotrifluoroethylene (δ = 145, 105, and 121 ppm). The chemical shifts of the remaining two resonances (δ = 73 and 57 ppm) are somewhat similar to those of the α -fluorine atoms in the perfluoropropenyl complexes of iron and manganese mentioned above. Moreover, the magnitude of the coupling (42 cps) between these two fluorine atoms indicates that they are *cis* to each other. The NMR data thus suggest structure (XIII) for the nickel compound.

The perfluorovinyl group is a simple example of a three-spin nuclear system. Hence in the F¹⁹ NMR spectrum of chlorotrifluoroethylene, where

the chemical shift differences between the three fluorine atoms are large compared with the spin coupling constants, there are three widely separated quartets, each corresponding to one of the three nonequivalent fluorine atoms. The F^{19} spectra of several perfluorovinyl derivatives of boron, silicon, germanium, tin, mercury, and arsenic have been reported (56). It might have been expected that the spectra, like that of chlorotrifluoroethylene, would be of the AMX type. Apparently this is so for several of the perfluorovinylmetal compounds when the spectra are recorded under moderate resolution. Under high resolution, however, the three quartets predicted by first order theory show further splitting. Long-range spin coupling between the fluorine atoms in different perfluorovinyl groups in compounds like $(CF_2:CF)_2Si(C_2H_5)_2$, $(CF_2:CF)_2Hg$, or $(CF_2:CF)_3As$ could perhaps be responsible for the hyperfine multiplet structures observed.

Little correlation was found between the F^{19} chemical shifts and the nature of the central atom in these perfluorovinyl derivatives, except for the boron compounds (56). In these compounds the shifts of fluorine atoms of the CF_2 group are relatively unshielded compared with the corresponding absorptions in the other perfluorovinyl compounds. This may reflect a mesomeric effect involving the vinyl group's π electrons and the boron atom.

B. Infrared Spectra

Fluorocarbon groups show very strong C—F absorptions in the 1400–1000 cm^{-1} region of the spectrum. This property has been extremely useful in the preparation of fluorocarbon–metal compounds. By examining the infrared spectrum of the reaction products it is possible to establish immediately whether the synthesis of a fluorocarbon derivative of a metal has been successful or not. The strong C—F absorptions reveal themselves immediately, even if the desired compound is diluted considerably with non-fluorine-containing material.

If a $CF_2:CF-M$ group ($M = B, Si, Ge, Sn, As, Hg$) is present in a molecule, a very distinctive series of four very strong absorptions occurs between 1750 and 1000 cm^{-1} (55). These bands have been assigned as follows: 1732–1695 cm^{-1} , $C=C$; 1327–1274 cm^{-1} , $=CF_2$ (asym.); 1178–1121 cm^{-1} , $=CF-$; 1049–1004 cm^{-1} , $=CF_2$ (sym). In vapor phase spectra these bands occur as single sharp peaks. However, in solution the $=CF_2$ (asym.) and $=CF-$ stretches appear as a doublet and triplet, respectively, while if liquid film spectra are recorded the $=CF_2$ (asym.), $=CF-$, and $=CF_2$ (sym.) absorptions are broad and usually sufficiently strong to be off scale.

The infrared spectral bands of many perfluorovinylmetal compounds are listed in refs. (37), (39), and (54), and especially in ref. (55). The strength of the C=C stretch is of some interest. When an ordinary unsubstituted vinyl group is σ -bonded to a metal the originally strong absorption due to the

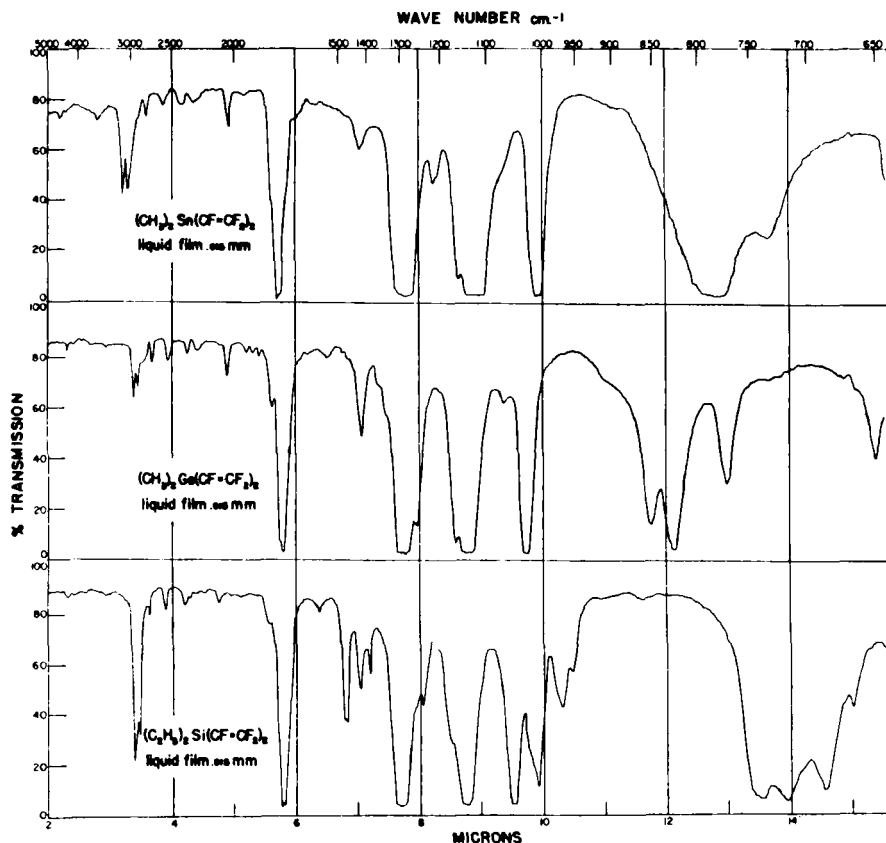


FIG. 3. Infrared spectra of some perfluorovinyl compounds. Reproduced with permission of the publisher. From *Spectrochim. Acta* **17**, 412 (1961).

C=C stretch, as it appears for example in vinyl chloride, is diminished, often to a point where its assignment becomes uncertain. In the case of the perfluorovinyl group there is no significant lessening of the intensity of the C=C absorption when the $\text{CF}_2\text{:CF-}$ group is bonded to a metal rather than to a hydrogen or halogen atom. Liquid film spectra of three perfluorovinyl derivatives are reproduced in Fig. 3.

The bands due to a $\text{CF}_3\text{—M}$ group are strikingly simple. Two very strong bands near 1140 and 1070 cm^{-1} are readily assigned to the carbon–fluorine stretching modes of the perfluoromethyl group (46). The C–F absorption bands in perfluoroethyl- and perfluoro-*n*-propylmetal compounds are more numerous (46, 155). The *n*- C_3F_7 group bonded to a metal gives rise to five characteristic infrared bands at $1335\text{--}1315$ (m), $1230\text{--}1215$ (s), $1205\text{--}1190$ (s), $1160\text{--}1150$ (m), and $1100\text{--}1085$ (m) cm^{-1} . The first three of these bands have been assigned to C–F stretches of the CF_3 group, while the two bands at lowest frequency have been attributed to C–F stretches of the $\beta\text{--CF}_2$ group (155). Bands due to the $\alpha\text{--CF}_2$ groups both in perfluoroethyl and in perfluoro-*n*-propyl compounds are more variable in frequency, appearing from $1050\text{--}990\text{ cm}^{-1}$. Some typical spectra over the range $1400\text{--}650\text{ cm}^{-1}$ taken with sodium chloride optics and using carbon disulfide solutions are given in Fig. 4. The medium to strong bands between 920 and 800 cm^{-1} have been assigned to the C–C stretching vibrations.

As expected fluorocarbon–transition metal carbonyls all show strong bands from about $2150\text{--}1980\text{ cm}^{-1}$ due to C–O stretches. Both the positions of these bands and their numbers are significant.

The C–O stretching frequencies in perfluoroalkyl or polyfluoroalkyl transition metal carbonyls are appreciably higher than those in alkyl transition metal carbonyls (155). Thus, for example, in $\text{CH}_3\text{Mn(CO)}_5$, C–O stretching bands occur at 2108 (m), 2010 (vs), and 1989 (s) cm^{-1} (155), while in $\text{HCF}_2\text{CF}_2\text{Mn(CO)}_5$ they appear at 2132 (m), 2045 (vs), and 2014 (s) cm^{-1} (97). The positions of these bands for $\text{HCF}_2\text{CF}_2\text{Mn(CO)}_5$ should be compared with those shown by $\text{Mn(CO)}_5\text{I}$ [2123 (m), 2045 (vs), and 2004 (s) cm^{-1}] (155, 156). It is generally observed that C–O stretching frequencies in the fluorocarbon–metal carbonyls are rather similar to those shown by the corresponding metal carbonyl halides (155). It is not surprising that the highly electronegative fluorocarbon groups have an effect similar to that of halogen atoms on the carbonyl frequencies. The rise in frequency on changing from an alkyl metal carbonyl to a fluoroalkyl metal carbonyl can be rationalized in terms of a greater removal of charge from the metal by the fluoroalkyl group in the latter class of complex. The metal electrons are thus less available for π bonding with the CO groups, so that for the metal–carbon bond the resonance hybrid $\text{M} \leftarrow \text{C} \equiv \text{O}$ becomes more important than the resonance hybrid $\text{M} = \text{C} = \text{O}$.

Perfluoroalkylmanganese and -rhenium pentacarbonyls display three major carbonyl stretching bands, consistent with the expected octahedral

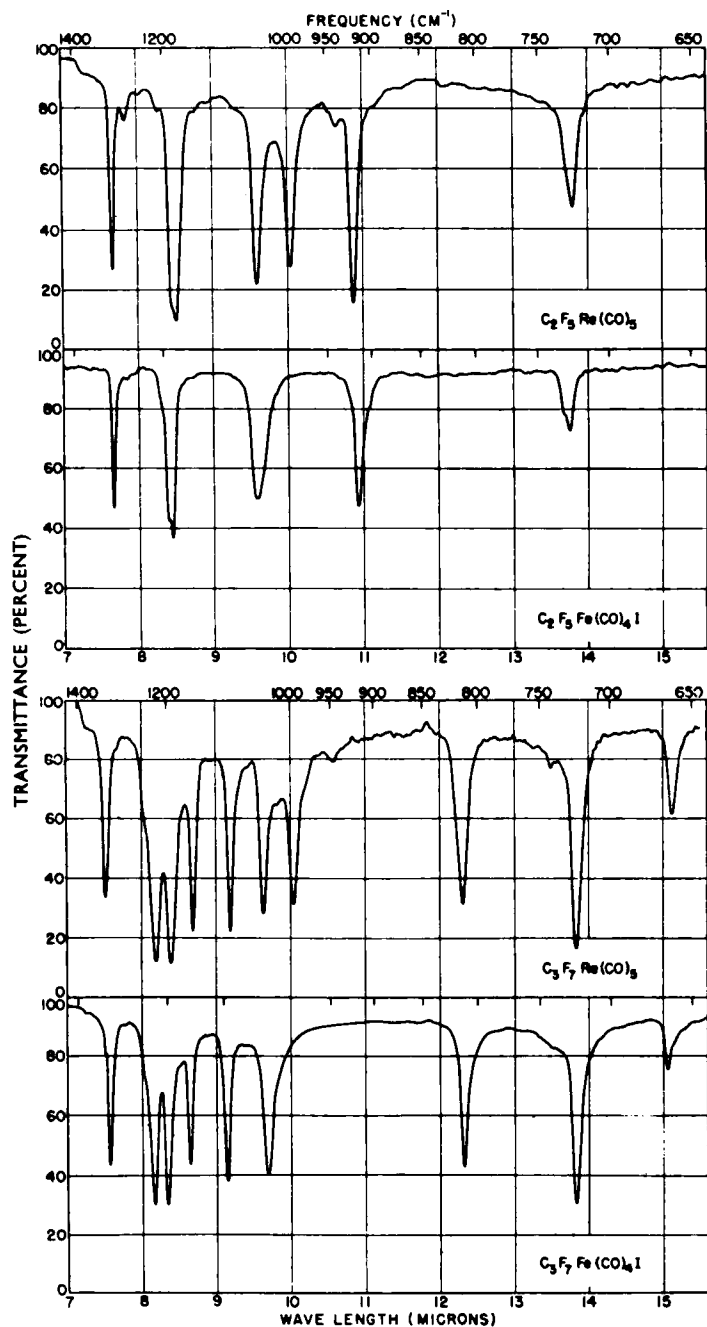


FIG. 4. Infrared spectra of some perfluoroalkyl transition metal carbonyls between 1400 and 650 cm^{-1} . Reproduced with permission of the publishers from *Spectrochim. Acta* **18**, 585 (1962).

structure of C_{4v} symmetry. The compound $(CF_2)_4Fe(CO)_4$ was originally said (130) to have C—O bands at 2160, 2120, and 2100 cm^{-1} but more recently four bands at 2160, 2108, 2088, and 2055 cm^{-1} have been reported (112). Four bands is the number expected for an octahedral structure (C_{2v}) in which the CF_2 groups bridge adjacent octahedral coordination positions of the iron atom. The bis(perfluoroalkyl)iron tetracarbonyls, $(R_F)_2Fe(CO)_4$, show several major carbonyl stretches. Four infrared active C—O stretches would be expected for a *cis* isomer and one for the *trans* isomer. Evidently, the *cis* isomers are present, and the presence of the *trans* isomer also cannot be ruled out (155). A similar conclusion can be made about the isomeric character of the perfluoroalkyliron tetracarbonyl iodides (155).

REFERENCES

1. H. J. Emeléus, *Angew. Chem. Intern. Ed.* **1**, 129 (1962).
2. H. J. Emeléus, *J. Chem. Soc.* p. 2979 (1954).
3. R. N. Haszeldine, *Roy. Inst. Chem. (London) Monograph* **1** (1956).
4. R. N. Haszeldine, *Angew. Chem.* **66**, 693 (1954).
5. R. E. Banks and R. N. Haszeldine, *Advan. Inorg. Chem. Radiochem.* **3**, 337 (1961).
- 5a. H. C. Clark, *Advan. Fluorine Chem.* **3**, 19 (1963).
6. H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.* p. 2948 (1949).
7. O. R. Pierce, E. T. McBee, and G. F. Judd, *J. Am. Chem. Soc.* **76**, 474 (1954).
8. J. A. Beel, H. C. Clark, and D. Whyman, *J. Chem. Soc.* p. 4423 (1962).
9. H. C. Clark and D. Whyman, *Proc. 2nd Intern. Meeting Fluorine Chem. Estes Park, Colorado, 1962* p. 232.
10. H. D. Kaesz and F. G. A. Stone, in "Organometallic Chemistry" (H. Zeiss, ed.), A.C.S. Monograph 147, Chapt. 3. Reinhold, New York, 1960.
11. D. Seyferth, *Progr. Inorg. Chem.* **3**, 129 (1962).
12. J. D. Park, R. J. Seffl, and J. R. Lacher, *J. Am. Chem. Soc.* **78**, 59 (1956).
13. I. L. Knunyants, R. N. Sterlin, R. D. Yatsenko, and L. N. Pinkina, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk.* p. 1345 (1958).
14. H. D. Kaesz, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.* **81**, 6336 (1959).
15. D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Letters* No. 22, 20 (1960).
16. D. Seyferth, D. E. Welch, and G. Raab, *J. Am. Chem. Soc.* **84**, 4266 (1962).
17. P. Tarrant, P. Johncock, and J. Savory, *J. Org. Chem.* **28**, 839 (1963).
18. S. Dixon, *J. Org. Chem.* **21**, 400 (1956).
19. P. L. Coe, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* p. 3227 (1962).
- 19a. A. G. Massey, A. J. Park, and F. G. A. Stone, *Proc. Chem. Soc.* p. 212 (1963).
- 19b. A. G. Massey, E. W. Randall, and D. Shaw, *Chem. Ind. (London)* p. 1244 (1963).
- 19c. P. M. Treichel, M. A. Chaudhari, and F. G. A. Stone, *J. Organometal. Chem.* **1**, 98 (1963).
20. R. N. Haszeldine, *J. Chem. Soc.* p. 1273 (1954).
21. A. L. Henne and W. C. Francis, *J. Am. Chem. Soc.* **73**, 3518 (1951).
22. O. R. Pierce and M. Levine, *J. Am. Chem. Soc.* **75**, 1254 (1953).
23. R. N. Haszeldine, *J. Chem. Soc.* p. 3423 (1952).

24. H. Normant, *Compt. Rend.* **239**, 1510 (1954).
25. H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint, and R. Cserr, *J. Org. Chem.* **22**, 1602 (1957).
26. R. N. Haszeldine, *J. Chem. Soc.* p. 1748 (1953).
27. O. R. Pierce, A. F. Meiners, and E. T. McBee, *J. Am. Chem. Soc.* **75**, 2516 (1953).
28. E. T. McBee, C. W. Roberts, and A. F. Meiners, *J. Am. Chem. Soc.* **79**, 335 (1957).
29. F. G. A. Stone and P. M. Treichel, *Chem. Ind. (London)* p. 837 (1960).
30. R. N. Sterlin, R. D. Yatsenko, and I. L. Knunyants, *Khim. Nauka i Prom.* **3**, 540 (1958); *Chem. Abstr.* **53**, 4194 (1959).
31. P. Tarrant and R. D. Richardson, *Abstr. Papers 138th Natl. Meeting Am. Chem. Soc. N.Y.* 1960 p. 17M (1960).
32. R. N. Sterlin, W.-K. Li, and I. L. Knunyants, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk.* 1506 (1959).
33. R. N. Sterlin, I. L. Knunyants, L. N. Pinkina, and R. D. Yatsenko, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk* p. 1492 (1959).
34. R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, and I. L. Knunyants, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk* p. 1991 (1960).
35. R. N. Sterlin, L. N. Pinkina, R. D. Yatsenko, and I. L. Knunyants, *Khim. Nauka i Prom.* **4**, 800 (1959); *Chem. Abstr.* **54**, 14104 (1960).
36. R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, and I. L. Knunyants, *Khim. Nauka i Prom.* **4**, 810 (1959); *Chem. Abstr.* **54**, 10838 (1960).
37. H. D. Kaesz, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 6232 (1960).
38. D. Seyferth, K. Brändle, and G. Raab, *Angew. Chem.* **72**, 77 (1960).
39. D. Seyferth, G. Raab, and K. A. Brändle, *J. Org. Chem.* **26**, 2934 (1961).
40. W. J. Pummer and L. A. Wall, *J. Res. Natl. Bur. Std.* **63A**, 167 (1959).
41. M. Hellmann, E. Peters, W. J. Pummer, and L. A. Wall, *J. Am. Chem. Soc.* **79**, 5654 (1957).
42. L. A. Wall, R. E. Donadio, and W. J. Pummer, *J. Am. Chem. Soc.* **82**, 4846 (1960).
43. E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.* p. 166 (1959).
44. A. B. Burg, 8th Ann. Tech. Rept. to the Office of Naval Research, Contract N6 onr-238-TO-I, November, 1954.
45. J. J. Lagowski and P. G. Thompson, *Proc. Chem. Soc.* p. 301 (1959).
46. H. D. Kaesz, J. R. Phillips, and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 6228 (1960).
47. J. Goubeau and K. H. Rohwedder, *Ann. Chem.* **604**, 168 (1957).
48. T. D. Parsons, E. D. Baker, A. B. Burg, and G. L. Juvinall, *J. Am. Chem. Soc.* **83**, 250 (1961).
49. B. Bartocha, W. A. G. Graham, and F. G. A. Stone, *J. Inorg. Nucl. Chem.* **6**, 119 (1958).
50. J. R. Phillips and F. G. A. Stone, *J. Chem. Soc.* p. 94 (1962).
51. J. M. Birchall, R. N. Haszeldine, and J. F. Marsh, *Chem. Ind. (London)* p. 1080 (1961).
52. T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 6223 (1960).
53. T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.* p. 3103 (1961).
54. S. L. Stafford and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 6238 (1960).
55. S. L. Stafford and F. G. A. Stone, *Spectrochim. Acta* **17**, 412 (1961).
56. T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *Spectrochim. Acta* **17**, 968 (1961).
57. R. D. Chambers, H. C. Clark, and C. J. Willis, *J. Am. Chem. Soc.* **82**, 5298 (1960).
- 57a. R. D. Chambers and T. Chivers, *Proc. Chem. Soc.* p. 208 (1963).
58. M. Hauptschein, A. J. Saggiomo, and C. S. Stokes, *J. Am. Chem. Soc.* **78**, 680 (1956).
59. B. Bartocha and A. J. Bilbo, *J. Am. Chem. Soc.* **83**, 2202 (1961).
60. D. Seyferth and T. Wada, *Inorg. Chem.* **1**, 78 (1962).

61. R. N. Haszeldine and J. C. Young, *J. Chem. Soc.* p. 4503 (1960).
62. A. M. Geyer and R. N. Haszeldine, *J. Chem. Soc.* p. 1038 (1957).
63. E. G. Rochow, *J. Am. Chem. Soc.* **67**, 963 (1945).
64. E. G. Rochow "An Introduction to the Chemistry of the Silicones," 2nd ed. Wiley, New York, 1951.
65. W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.* **84**, 3599 (1962).
66. R. N. Haszeldine, M. J. Newlands, and J. B. Plumb, *Proc. Chem. Soc.* p. 147 (1960).
67. R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.* p. 394 (1959).
68. D. Seyferth, T. Wada, and G. E. Maciel, *Inorg. Chem.* **1**, 232 (1962).
69. R. Meier and F. Böhrer, *Chem. Ber.* **90**, 2344 (1957).
70. T. F. McGrath and R. Levine, *J. Am. Chem. Soc.* **77**, 4168 (1955).
71. G. Bier and H. Fritz, German patent 1,006,852 (1957); *Chem. Abstr.* **53**, 18862 (1959).
72. H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.* **84**, 898 (1962).
73. H. D. Kaesz, J. R. Phillips, and F. G. A. Stone, *Chem. Ind. (London)* p. 1409 (1959).
74. R. D. Chambers, H. C. Clark, and C. J. Willis, *Chem. Ind. (London)* p. 76 (1960).
75. H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.* **82**, 1888 (1960).
76. M. A. A. Beg and H. C. Clark, *Chem. Ind. (London)* p. 140 (1962).
77. H. G. Kuivila and E. R. Jakusik, *J. Org. Chem.* **26**, 1426 (1961).
- 77a. J. M. Holmes, R. D. Peacock, and J. C. Tatlow, *Proc. Chem. Soc.* p. 108 (1963).
78. C. G. Krespan and V. A. Engelhardt, *J. Org. Chem.* **23**, 1565 (1958).
- 78a. H. C. Clark, S. Furnival, and J. T. Kwon, *Abstr. 1st Intern. Conf. Organometallic Chem. Cincinnati, Ohio, 1963*.
79. D. Seyferth, *J. Am. Chem. Soc.* **79**, 2133 (1957).
80. F. E. Brinckman and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 6218 (1960).
81. A. B. Burg and J. R. Spielman, *J. Am. Chem. Soc.* **83**, 2667 (1961).
82. R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.* **60**, 459 (1960), and references cited therein.
83. D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.* **83**, 3583 (1961).
84. D. Seyferth, *J. Org. Chem.* **22**, 478 (1957).
85. A. Saitow, E. G. Rochow, and D. Seyferth, *J. Org. Chem.* **23**, 116 (1958).
86. H. H. Jaffe and G. O. Doak, *J. Chem. Phys.* **21**, 196 (1953).
87. J. Chatt and B. L. Shaw, *J. Chem. Soc.* pp. 705, 4020 (1959); p. 1718 (1960); p. 285 (1961).
88. J. Chatt, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)* **21**, 147 (1960).
89. J. J. Lagowski, *Quart. Rev. (London)* **13**, 233 (1959).
90. J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.* **84**, 3442 (1962).
91. H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.* **15b**, 763 (1960).
92. T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.* **83**, 249 (1961).
93. R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.* **22**, 598 (1957).
94. T. H. Coffield, J. Kozikowski, and R. D. Closson, *Abstr. 5th Intern. Conf. Coordination Chem. London 1959, Chem. Soc. (London) Spec. Publ.* **13**, 126 (1959).
95. W. R. McClellan, *J. Am. Chem. Soc.* **83**, 1598 (1961).
96. W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.* **94**, 862 (1961).
97. P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.* **1**, 511 (1962).
- 97a. R. B. King, *J. Am. Chem. Soc.* **85**, 1922 (1963).
98. R. B. King, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.* p. 69 (1961).
99. R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.* **83**, 3604 (1961).
100. W. Hieber, W. Beck, E. Lindner, *Z. Naturforsch.* **16b**, 229 (1962).

101. W. Hieber and E. Lindner, *Chem. Ber.* **95**, 2042 (1962).
102. P. W. Jolly and F. G. A. Stone, unpublished observations.
- 102a. D. W. McBride, E. Pitcher, and F. G. A. Stone, *J. Chem. Soc.* in press.
- 102b. R. B. King, *J. Am. Chem. Soc.* **85**, 1918 (1963).
103. K. A. Keblyns and A. H. Filbey, *J. Am. Chem. Soc.* **82**, 4204 (1960).
104. F. A. Cotton and F. Calderazzo, *Inorg. Chem.* **1**, 30 (1962).
105. R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.* **83**, 3593 (1961).
106. F. G. A. Stone, D. W. McBride, E. Pitcher, R. A. Plowman, and P. M. Treichel, *Proc. 2nd Intern. Meeting Fluorine Chem, Estes Park, Colorado, 1962* p. 192 (1962).
107. D. W. McBride, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.* p. 723 (1963).
108. J. Chatt and F. A. Hart, *J. Chem. Soc.* p. 1378 (1960).
109. K. F. Watterson and G. Wilkinson, *Chem. Ind. (London)* p. 1358 (1960).
110. T. D. Coyle, R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.* **20**, 172 (1961).
111. J. R. Phillips, Ph.D. Thesis, Harvard Univ., Cambridge, Massachusetts, 1962.
112. H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.* p. 2738 (1961).
113. P. M. Treichel, J. Morris, and F. G. A. Stone, *J. Chem. Soc.* p. 720 (1963).
114. M. L. H. Green, private communication.
115. R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.* **83**, 4023 (1961).
116. J. Chatt and B. L. Shaw, *J. Chem. Soc.* p. 5075 (1962).
117. J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.* p. 218 (1963).
118. D. W. A. Sharp and R. D. W. Kemmitt, private communication.
119. E. Pitcher and F. G. A. Stone, *Spectrochim. Acta* **17**, 1244 (1961).
120. P. M. Maitlis and F. G. A. Stone, *Chem. Ind. (London)* p. 1865 (1962).
121. G. E. Coates, "Organometallic Compounds," p. 319. Methuen, London, 1960.
- 121a. A. J. Berthold and G. Groh, *Angew. Chem. Intern. Ed.* **2**, 398 (1963).
122. A. G. Massey, A. J. Park, P. M. Treichel, J. B. Wilford, and F. G. A. Stone, *Abstr. I.U.P.A.C., London, 1963* p. 192.
123. D. W. McBride, Ph.D. Thesis, Harvard Univ., Cambridge, Massachusetts, 1962.
124. P. M. Treichel, unpublished observations.
125. R. A. Plowman and F. G. A. Stone, *Inorg. Chem.* **1**, 518 (1962).
126. T. A. Manuel, *Inorg. Chem.* **2**, 854 (1963).
127. R. F. Heck and D. S. Breslow, in "Advances in the Chemistry of Coordination Compounds" (S. Kirschner, ed.), p. 281. Macmillan, New York, 1961.
128. H. W. Sternberg and I. Wender, *Chem. Soc. (London) Spec. Publ.* **13**, 50 (1959).
129. R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.* **82**, 4438 (1960).
130. K. F. Watterson and G. Wilkinson, *Chem. Ind. (London)* p. 991 (1959).
131. P. L. Pauson, *Proc. Chem. Soc.* p. 297 (1960).
132. R. G. Guy and B. L. Shaw, *Adv. Inorg. Chem. Radiochem.* **4**, 77 (1962).
133. D. L. Smith and L. F. Dahl, *J. Am. Chem. Soc.* **84**, 1743 (1962).
134. G. W. Parshall and G. Wilkinson, *J. Chem. Soc.* p. 1132 (1962).
135. J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *Chem. Ind. (London)* p. 1358 (1960).
136. J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.* p. 3488 (1962).
137. H. Greenfield, H. W. Sternberg, R. A. Friedel, J. Wotiz, R. Markby, and I. Wender, *J. Am. Chem. Soc.* **78**, 120 (1956).
138. W. G. Sly, *J. Am. Chem. Soc.* **81**, 18 (1959).
139. J. F. Tilney-Bassett and O. S. Mills, *J. Am. Chem. Soc.* **81**, 4757 (1959).
140. J. F. Tilney-Bassett, *J. Chem. Soc.* p. 577 (1961).

- 140a. W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc.* p. 169 (1961).
141. M. Dubeck, *J. Am. Chem. Soc.* **82**, 6193 (1960).
142. E. Weiss and W. Hubel, *J. Inorg. Nucl. Chem.* **11**, 42 (1959).
- 142a. M. R. Churchill, M. Gerloch, and R. Mason, *Proc. Chem. Soc.* p. 107 (1963).
143. D. W. McBride, R. L. Pruett, E. Pitcher, and F. G. A. Stone, *J. Am. Chem. Soc.* **84**, 497 (1962).
144. R. N. Haszeldine and E. G. Walaschewski, *J. Chem. Soc.* p. 3607 (1953).
145. W. T. Miller, E. Bergman, and A. H. Fainberg, *J. Am. Chem. Soc.* **79**, 4159 (1957).
146. R. N. Haszeldine, *Nature* **168**, 1028 (1951).
147. C. G. Krespan, *J. Org. Chem.* **25**, 105 (1960).
148. H. Goldwhite, R. N. Haszeldine, and R. N. Mukherjee, *J. Chem. Soc.* p. 3825 (1961).
- 148a. P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, *J. Org. Chem.* **28**, 184 (1963).
149. H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.* p. 2953 (1949).
150. H. J. Emeléus and J. J. Lagowski, *J. Chem. Soc.* p. 1497 (1959).
- 150a. H. B. Powell, M. T. Maung, and J. J. Lagowski, *J. Chem. Soc.* p. 2484 (1963).
151. R. D. Chambers, G. E. Coates, J. G. Livingstone, and W. K. R. Musgrave, *J. Chem. Soc.* p. 4367 (1962).
152. R. D. Chambers, H. C. Clark, L. W. Reeves, and C. J. Willis, *Canad. J. Chem.* **39**, 258 (1961).
153. E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.* **36**, 124 (1962).
- 153a. A. J. Bourn, D. Gillies, and E. W. Randall, *Proc. Chem. Soc.* p. 200 (1963).
154. R. D. Chambers, H. C. Clark, and C. J. Willis, *Canad. J. Chem.* **39**, 131 (1961).
155. E. Pitcher and F. G. A. Stone, *Spectrochim. Acta* **18**, 585 (1962).
156. M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry* **9**, 310 (1962).

Conjugate Addition of Grignard Reagents to Aromatic Systems

REYNOLD C. FUSON

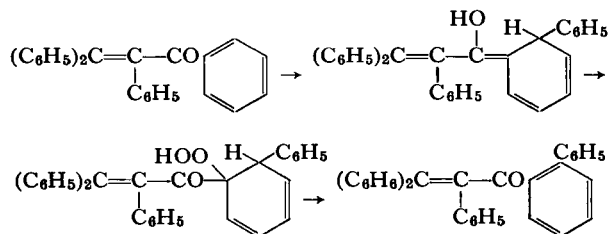
Center for Advanced Study, University of Illinois
Urbana, Illinois

I. Early Examples	221
II. Polycyclic Ketones	223
III. Hindered Ketones	228
IV. Heterocyclic Compounds	232
V. Phenolic Ketones	235
References	237

I

EARLY EXAMPLES

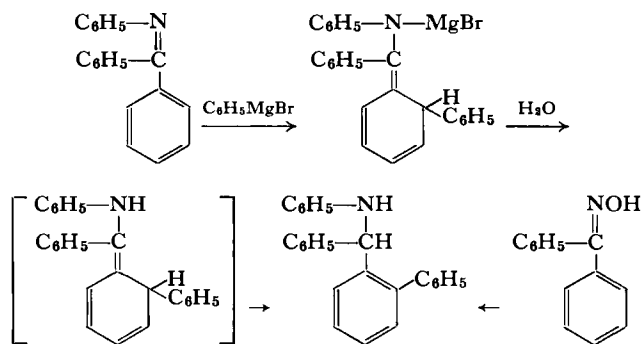
Twenty-six years after his discovery of 1,4-addition of phenylmagnesium bromide to benzalacetophenone (1) Kohler, working with Nygaard, extended this type of reaction to aromatic systems (2). When they treated tetraphenylpropene-one with the phenyl reagent under ordinary conditions, no reaction was observed. Condensation was effected, however, by adding benzene to the reaction mixture and distilling ether until the boiling point of the mixture rose to 50–52° C. Under these “forcing” conditions both 1,2- and 1,4-addition occurred, but the 1,4-addition product, obtained in 37% yield, was not that expected. It proved to be an enol, which when exposed to oxygen formed a peroxide.



When the peroxidic substance, which we now regard as a hydroperoxide (3), was treated with sodium methoxide it lost the elements of hydrogen peroxide to yield the aromatized ketone phenylated in an *o*-position. 1,4-Addition had indeed occurred and involved, not the lateral olefinic bond, but instead a bond of the phenyl nucleus. The failure of the lateral double bond to enter into reaction may be ascribed to a combination of unfavorable electronic and steric influences.

Reaction of methylmagnesium iodide with tetraphenylpropenone, surprisingly, proceeded only in the 1,2-manner; in other cases in which both types of addition are possible, the amount of 1,4-addition product had always been found to be greater with alkyl than with aryl Grignard reagents.

The discovery of Kohler and Nygaard, which they called "unlocking the benzene ring," was not the first of the type, however. That conjugate addition of Grignard reagents may occur in such a way as to involve an aromatic ring had been demonstrated by Gilman *et al.* (4), who in the preceding year had added phenylmagnesium bromide in the 1,4-manner to the anil of benzophenone. The reaction was conducted at a temperature of 90–100° C in a mixture of ethyl ether and toluene, i.e., under forcing conditions. It would appear that the enamine formed initially rearranged in such a way as to restore the aromaticity of the benzene ring that was phenylated; the yield was 42%.

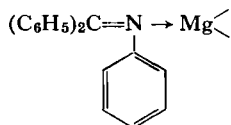


It is extremely interesting that the same product, *o*-phenylbenzohydryl-aniline, was obtained also from phenyl isocyanate, from phenyl isothiocyanate and—as shown by Campbell in 1932—from the oxime of benzophenone (5).

Later benzophenone β -naphthyl was found by Gilman and Morton (6) to react with phenylmagnesium bromide in a similar way. Under forcing con-

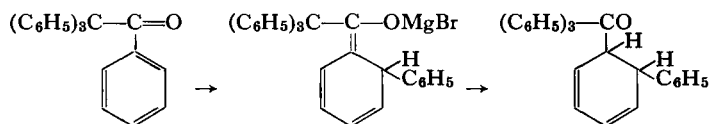
ditions condensation occurred, the product being *o*-phenylbenzohydril- β -naphthylamine. Phenyllithium reacted readily and in the 1,2-manner with these anils (7).

One can picture a coordination product formed by the Grignard reagent, acting as a Lewis acid, and the anil in which the carbon atom of the azomethine group is flanked by a phenyl radical on one side and by a molecule of Grignard reagent on the other.



The Grignard reagent coordinates with the oxygen atom of a ketone, thus enhancing the electron deficiency at the carbonyl carbon atom. When ethylmagnesium bromide is added to Michler's ketone, for example, in such a way that the ketone is always present in excess, no condensation occurs and the ketone is almost completely regenerated by treatment of the coordination complex with water (8).

We now know that the benzene ring had been "unlocked" twenty years before the discoveries of Gilman *et al.*, and of Kohler and Nygaard. In 1910 Schmidlin and Wohl added phenylmagnesium bromide to β -benzopinacolone and obtained what they thought to be pentaphenylethanol (9). It remained for Mosher and Huber in 1953 to recognize the true nature of the product; they gave convincing evidence that the compound was, instead, the dihydro ketone formed by 1,4-addition (10).



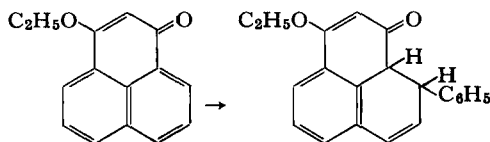
The interesting pentaphenylethanol, therefore, remained an unknown substance until recently (10a).

II

POLYCYCLIC KETONES

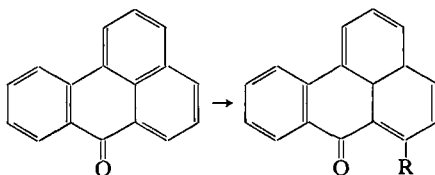
Three years after the paper of Schmidlin and Wohl was published Calderaro reported 1,2-addition of the phenyl reagent to 3-ethoxy-1-benzonaphthen-1-one (11). The reaction, as was shown later by Koelsch

and Rosenwald (12), was of the 1,4-type instead and involved an aromatic ring.



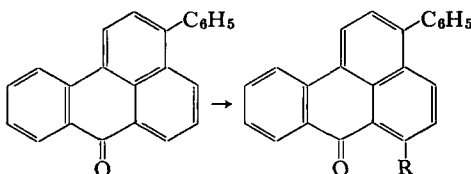
These authors showed that 3-methoxy-2-phenyl-1-benzonaphthen-1-one behaved in a similar way (13).

Benzanthrone likewise combined with Grignard reagents; both Clar (14) and Nikanishi (15) believed that they had brought about 1,6-addition. Charrier and Ghigi showed, however, that the reaction was of the 1,4-type. With the methyl and ethyl reagents the corresponding 4-alkyl derivatives of benzanthrone were obtained (16).



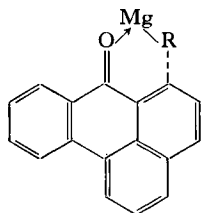
In a more extended study of this type of reaction Allen and Overbaugh introduced the following radicals into the 4-position (17): phenyl (42%), benzyl (22%), *n*-heptyl (61%), and cyclohexyl (15%).

Similarly by 1,4-addition to *bz*-1-phenylbenzanthrone the benzyl (19%), phenyl (45%), phenethyl (51%), cyclohexyl (22%), ethyl (35%), *n*-butyl (53%), *n*-hexyl (47%), and styryl (6%) derivatives were produced (18).

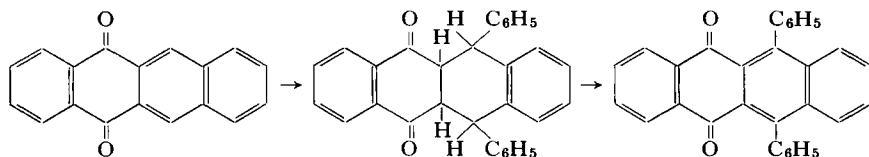


It has been pointed out that in the coordination complex the hydrocarbon radical of the reagent may be very near the 4-position, and the postulate has been put forward that 1,4-addition involves a *quasi*-six-membered ring in the transition state. On this assumption it would be predicted that in-

creasing rigidity of the elements making up the *quasi*-six-membered ring would favor 1,4-addition. The fact that benzanthrone is rigidly planar thus may be presumed to favor conjugate addition.

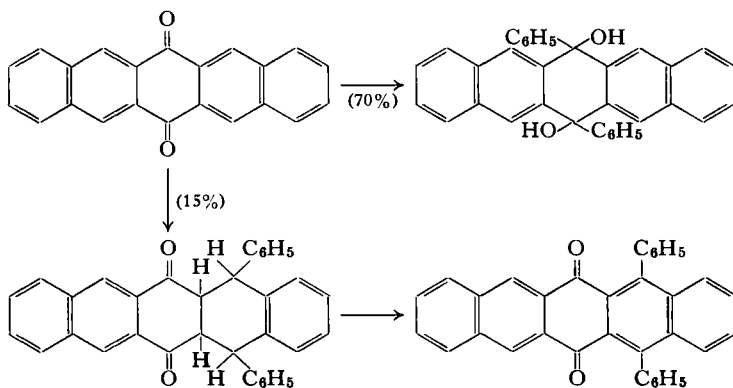


In benzanthrone the carbonyl group is attached on one side to a benzene nucleus and on the other to a naphthalene nucleus, and it seems probable that the ease of conjugate addition in these examples is to be ascribed to the high order of double bond quality exhibited by the 1,2-bond in naphthalene. The same structural feature is present in naphthacenequinone which was found by Allen and Gilman (19) and by Dufraisse and Horclois (20) to undergo a double 1,4-addition reaction with phenylmagnesium bromide. Addition of the second molecule of reagent would be expected to be easy since the ring involved is no longer benzenoid.

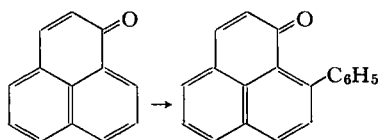


Diphenylnaphthacenequinone did not combine with phenylmagnesium bromide but gave the expected dihydroxy compound with phenyllithium. It is to be noted that anthrone and anthraquinone, having only benzene nuclei, fail to react with phenylmagnesium bromide in the conjugate manner. Moreover naphthacenequinone which, like benzanthrone, has the benzene and naphthalene nuclei in competition with one another is vulnerable only in the naphthalene nucleus.

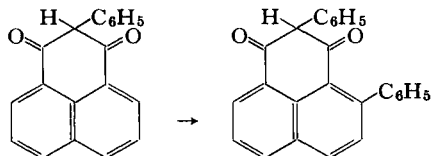
Very similar results were obtained by Allen and Bell with 6,13-pentacenequinone, which has two naphthalene nuclei (21). Condensation with the phenyl reagent gave the normal diol in a yield of 70% whereas the 1,4-addition product was obtained in 15% yield.



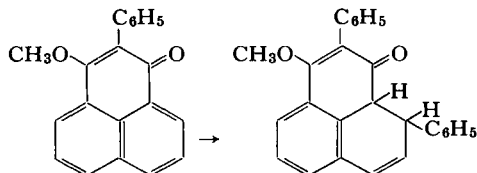
Much more remarkable is the similar condensation, discovered by Koelsch and Anthes, of phenylmagnesium bromide with 1-benzonaphthen-1-one (22). The product underwent dehydrogenation to yield 9-phenyl-1-benzonaphthene-1-one.



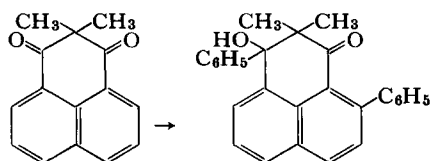
Conjugate addition involving an aromatic ring was observed by Koelsch and Rosenwald with 2-phenyl-1-benzonaphthene-1,3-dione (13). The diketone obtained by dehydrogenation of the product was shown to be the 2,9-diphenyl diketone.



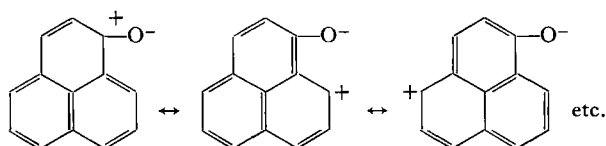
Phenyllithium was used as the reagent, however. The methyl ether reacted in a similar way with phenylmagnesium bromide.



2,2-Dimethyl-1-benzonaphthen-1,3-dione was found by Geissman and Morris to undergo both 1,2- and 1,4-addition with the phenyl reagent (23).

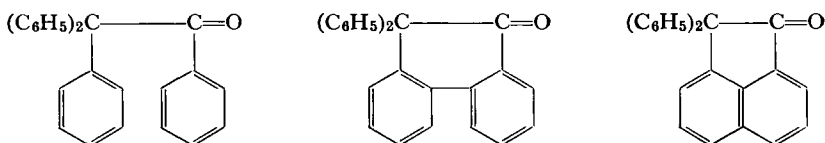


It should be pointed out that in such ketones the positive charge may be delocalized to the other rings.

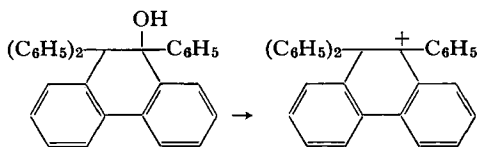


Even in the case of the simple benzonaphthene derivatives it is exceedingly difficult to determine which ring may be properly designated as the *peri* ring (24).

An interesting series is formed by β -benzopinacolone, 10,10-diphenyl-9,10-dihydro-9-phenanthrene, and 9,9-diphenylacenaphenone.



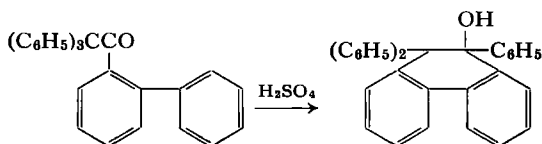
Treatment of the phenanthrone with the phenyl reagent gave both 1,2- and 1,4-addition products (25). The carbinol formed by 1,2-addition had been made earlier from the phenanthrone and phenyllithium (26). This alcohol was recovered after being treated with sulfuric acid, which must mean that the corresponding carbonium ion does not undergo rearrangement.



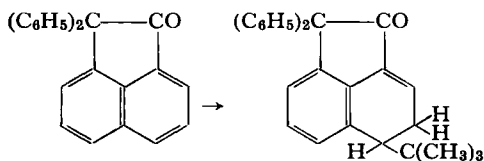
It was concluded also that the isomeric carbonium ions, which might have been formed by rearrangement, would prove to be less stable.



This deduction is supported by the observation of Mosher and Huber that 2-biphenyltriphenylmethyl ketone undergoes rearrangement in the presence of sulfuric acid to the phenanthrol derivative.



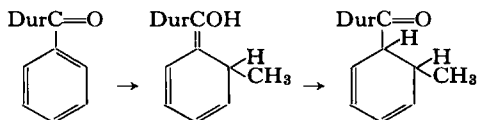
9,9-Diphenylacenaphthenone was found to react in the conjugate manner with *t*-butylmagnesium chloride to give chiefly the 1,6-addition product (27).



III

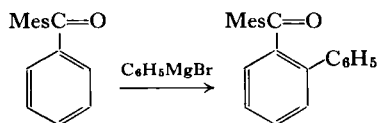
HINDERED KETONES

The nearly prohibitive hindrance in mesityl ketones makes it possible to effect conjugate addition involving a benzene ring. Even the methyl reagent is capable of adding in the conjugate manner. An example is 1,4-addition of methylmagnesium iodide to duryl phenyl ketone to give duryl 2-methyl-1,2-dihydrophenyl ketone (28).

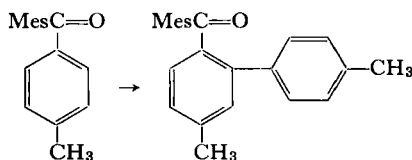


Products resulting from 1,2- and 1,6-addition were also isolated.

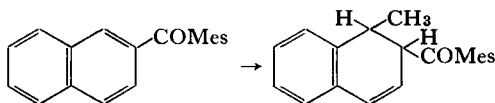
The first conjugate addition reaction to be observed in this series was with mesityl phenyl ketone and the phenyl reagent. The product, obtained in a yield of 18%, was 2-mesitylbiphenyl (29).



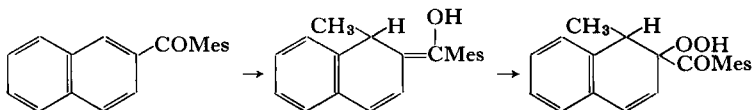
Mesityl *p*-tolyl ketone and *p*-tolylmagnesium bromide gave a similar result.



Here again the naphthalene nucleus proved to be more reactive than the benzene ring. The condensation product from mesityl 2-naphthyl ketone and the methyl reagent, obtained in a yield of 74%, was 2-mesityl-1-methyl-1,2-dihydronaphthalene (30).



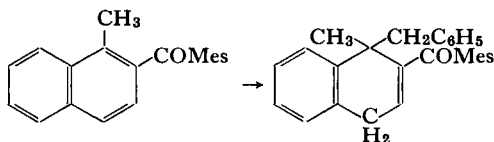
A similar condensation was realized with mesityl 1-naphthyl ketone and the phenyl reagent. The intermediate formation of the enol was demonstrated in the condensation of methylmagnesium iodide with mesityl 2-naphthyl ketone; the hydroperoxide was obtained in a yield of 74% (30).



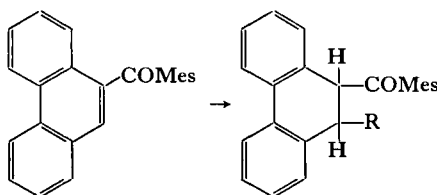
It seems probable that the examples of *p*-alkylation likewise involve enolic intermediates corresponding to 1,6-addition, but conclusive evidence for this view is lacking at present.

A much more remarkable reaction took place when 1-methyl-2-mesitylnaphthalene was treated with benzylmagnesium chloride in boiling ethyl

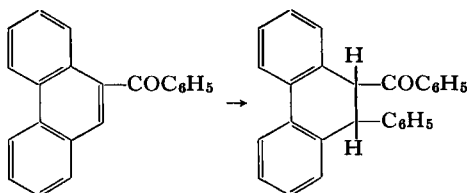
ether. Although the 4-position already held a methyl group, which might reasonably be expected to oppose the entrance of a second radical, the benzyl group nonetheless was found to enter this position (31).



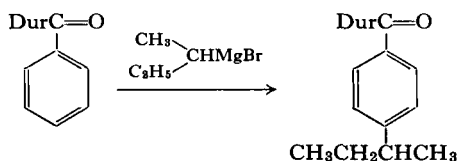
9-Phenanthryl mesityl ketone was found to react in the 1,4-manner with the methyl and phenyl reagents (32).



The unhindered ketone, 9-phenanthryl phenyl ketone, also underwent 1,4-addition with the phenyl reagent (32).



Success with such reactions became much more marked when it was realized that the methyl and phenyl organometallic compounds are not the reagents of choice for conjugate addition reactions of the type under discussion. Stevens had already shown the superiority of the *t*-butyl reagent (33) and, with the aid of the table of electronegativities of Kharasch and Weinhouse (34), it was possible to deduce that the benzyl, cyclohexyl, isopropyl, *sec*-butyl, and similar reagents would also be very effective. The result with *sec*-butyl magnesium bromide is illustrative. With duryl phenyl ketone it gave *p*-*sec*-butylphenyl duryl ketone in a 63% yield (35).

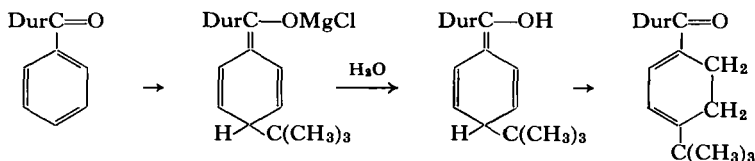


Actually the first *p*-alkylation to be effected involved the benzyl reagent; the yield of *p*-benzylphenyl duryl ketone was only 22%, however (36.)

It will be recalled that the reagents that are effective here are of the same type as those found to be capable of reacting additively with fulvenes (37).

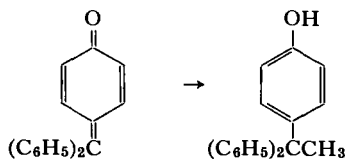
p-Alkylation reactions are remarkable in several ways. In the first place, they proceed readily in ordinary ether. Also, the alkylation occurs at the *p*-position in spite of the fact that both *o*-positions are unoccupied. The reaction corresponds to 1,6-addition, which is rarely observed with Grignard reagents, yet the product is fully aromatic.

Aromatization proved to have been produced by access of air to the reaction mixture. When prepared under nitrogen the product was the dihydro compound. Deliberate introduction of oxygen before hydrolysis gave the fully aromatic ketone (38).

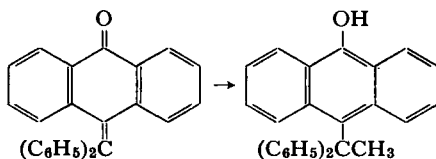


It may be pointed out that, whereas coordination with the carbonyl oxygen atom as well as attack at the 2- and 4-positions might be accomplished by a single molecule of the Grignard reagent, reaction at the *p*-position would seem to require the intervention of a second molecule of the organomagnesium compound.

This type of 1,6-addition destroys the aromaticity of the ring that is attacked and is very different from 1,6-addition of Grignard reagents to ketones of the fuchsone type in which a new aromatic ring is generated. Fuchsone itself was reported by Baeyer and Villiger to combine with methylmagnesium iodide in the 1,6-manner (39).



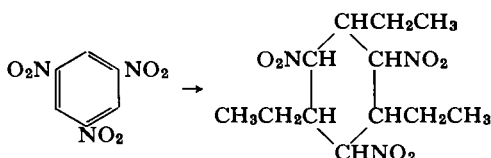
It remained for Julian and Gist (40) to establish the structure of the product, however; these authors found that α -naphthofuchson behaves in a similar way.



This mode of addition of Grignard reagents had been observed earlier with methyleneanthrone (41).

It might be expected that the vulnerability of the benzene ring of a hindered ketone would be increased by a second ketone group, especially if placed in a position *meta* to the first. Experiments with *m*-dimesitylbenzene have confirmed this expectation; with the methyl, benzyl, and phenyl reagents double addition occurred (42).

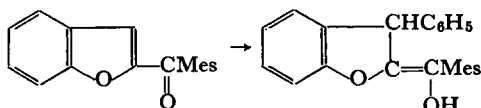
Triple addition has been reported for 1,3,5-trinitrobenzene and the ethyl reagent; the product is 1,3,5-triethyl-2,4,6-trinitrocyclohexane (43).



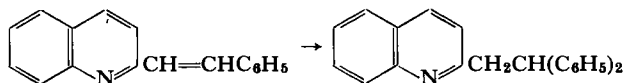
IV

HETEROCYCLIC COMPOUNDS

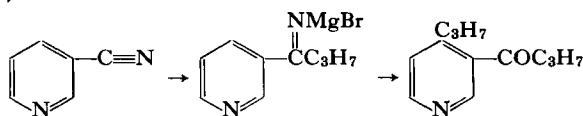
Addition of Grignard reagents to conjugated systems involving heterocyclic aromatic nuclei is known also. Although 2-benzoylfuran condensed normally with Grignard reagents to yield carbinols, the corresponding hindered ketones reacted in the conjugate manner, the furan ring being attacked. 2-Mesitylbenzofuran, for example, combined with phenylmagnesium bromide to give the enol form of 2-mesityl-3-phenyl-2,3-dihydrobenzofuran (44). 2-(2,4,6-Triisopropyl)benzoylfuran appeared to behave in a similar manner.



Aromatic heterocyclic nitrogen compounds likewise reacted with Grignard reagents in the conjugate manner. An example is the condensation of the phenyl reagent with benzalquinaldine. The product, α -benzohydryl-quinaldine, was obtained in a yield of 70% (45).



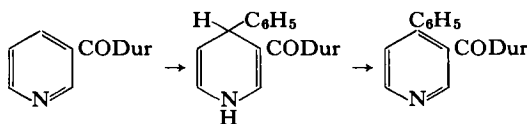
The action of the *n*-propyl reagent on nicotinonitrile provided a similar example (46).



Evidently, in the imino derivative that must be assumed as an intermediate, the crossed conjugated system favors attack at the 4-position. Comparison with the anils of diaryl ketones, suggests that the following anils would be especially sensitive to attack.

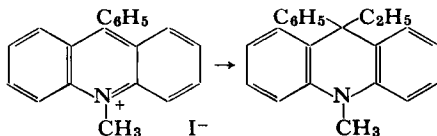


1,4-Addition has been realized with 3-duroylpyridine; the dihydro products have been aromatized (47).



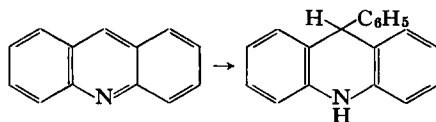
Similar behavior has been observed with the corresponding mesitoyl and benzoyl compounds as well as with 3-benzoyl- and 3-mesitylquinoline (47).

9-Phenylacridine methiodide reacted with ethylmagnesium bromide to give 9-ethyl-10-methyl-9-phenyl-9,10-dihydroacridine (48).

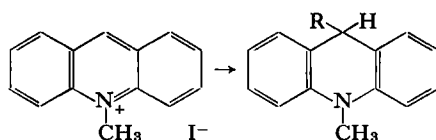


9-Ethylacridine behaved in a similar way (49).

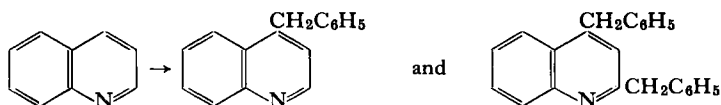
Acridine itself reacted with the phenyl reagent to give 9-phenylacridine, presumably by way of the dihydro derivative (50).



The methiodide reacted with Grignard reagents to give the corresponding 10-substituted-9,10-dihydroacridines (49).

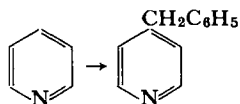


The benzyl reagent and quinoline have been reported to give a mixture of the 4-benzyl and the 2,4-dibenzyl derivatives (51).

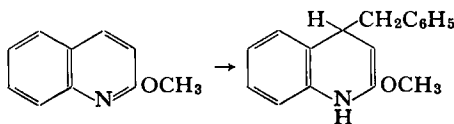


In view of the addition of phenyllithium to the 1,2-position of 2-phenylquinoline (52) the identity of the dibenzylquinoline might be questioned (53).

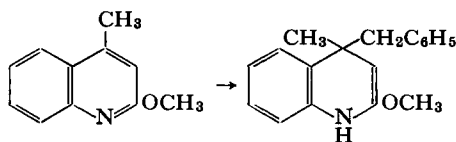
Of particular interest here is the behavior of pyridine toward the benzyl reagent since the principal product was 4-benzylpyridine (54).



2-Methoxyquinoline behaved in a similar way; the methoxyl group was not attacked, as might have been expected on the basis of the similarity of the compound to an ester. The product, 4-benzyl-2-methoxydihydroquinoline, was assumed to have the 1,4-dihydro structure. However, the 3,4-dihydro structure is also a possibility (55).



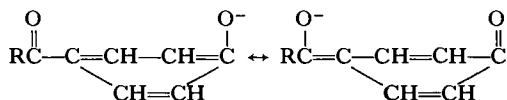
It is even more surprising that 2-methoxyepidine, in which the 4-position is blocked, likewise underwent 1,4-addition.



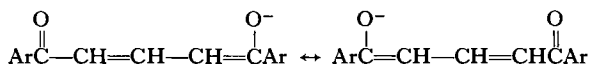
V

PHENOLIC KETONES

One of the most remarkable reactions that has been encountered in this field is the addition of Grignard reagents to phenolic ketones. Here we are dealing with phenoxide ions, which are vinylogs of the corresponding carboxylate ions.

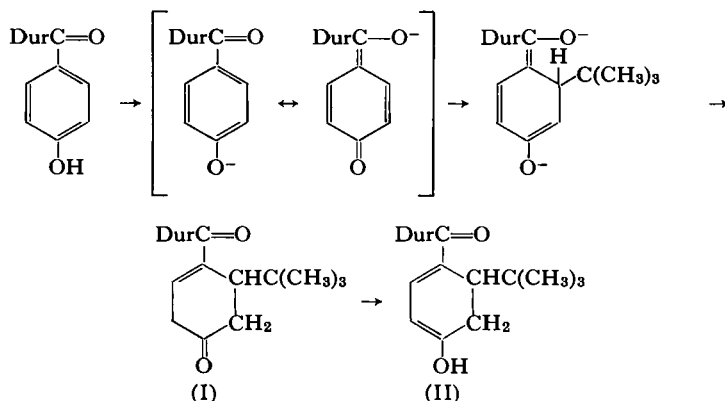


Except that they contain rings, they are closely analogous to the 1,5-diaryl-pentadienolonates (56).



The analogy implies that the phenoxide ions are vulnerable to nucleophilic attack at a position *ortho* to the keto substituent. This prediction has been verified experimentally by treating *p*-duroylphenol with Grignard reagents. This hydroxy ketone reacted with *t*-butylmagnesium chloride to give 6-*t*-butyl-4-keto-1-cyclohexenyl duryl ketone (I) in a yield of 75% (57).

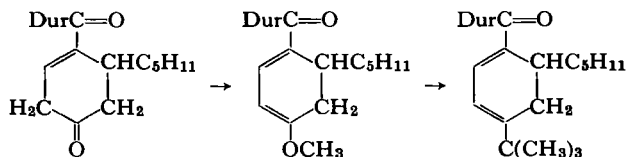
The diketone, recrystallized from high-boiling petroleum ether, was colorless and melted at 158.5–159° C. When the recrystallization solvent was methanol or ethanol, however, the enolic tautomer, 2-*t*-butyl-4-hydroxy-2,3-dihydrophenyl duryl ketone (II, m.p. 173–173.5° C), was produced. These tautomers were found to be stable in the solid state and were readily interconvertible. The enol, obtained by recrystallizing the diketone from polar solvents, could be reconverted to the diketone simply by recrystallization from nonpolar solvents such as benzene or petroleum ether. Prolonged boiling with the nonpolar solvent was necessary since the enol appeared to be only slightly soluble in such media. This observation is similar to that of



Russell, who found that the concentration of enol in solutions of certain β -ketonitriles is greater in polar than in nonpolar solvents (58). As would be expected, either form will serve in the preparation of derivatives such as the oxime of the diketone and the acetate of the enol. This example of tautomerism is remarkable, especially because the enol cannot form chelates.

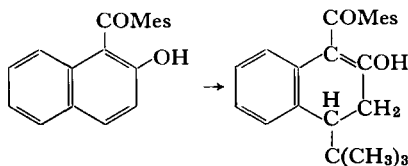
It is interesting that, whereas esterification of duroic acid is not effected by the Victor Meyer method, its vinylog, the enol, underwent etherification under these conditions. Heating with methanol in the presence of hydrogen chloride sufficed to convert it into the methyl ether, which in turn is a vinylog of an ester. The enol ether was "saponified" by aqueous sodium hydroxide, the salt of the enol being formed.

t-Amylmagnesium chloride reacted with *p*-duroylphenol in much the same manner as the *t*-butyl reagent to give 6-*t*-amyl-4-keto-1-cyclohexenyl duryl ketone. Like the *t*-butyl analog, this ketone gave a methyl enol ether when treated with methanol and hydrogen chloride. Displacement of the methoxyl group by *t*-butylmagnesium chloride gave 2-*t*-amyl-4-*t*-butyl-2,3-dihydrophenyl duryl ketone.

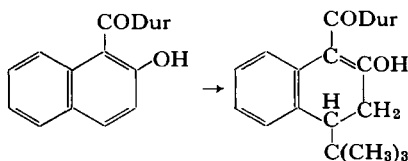


As was to be expected, the addition of Grignard reagents to phenoxides could be extended to the naphthalene series. 2-Hydroxy-1-mesitylnaphthalene, for example, reacted with *t*-butylmagnesium chloride to give

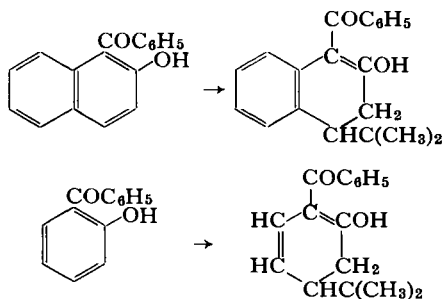
4-*t*-butyl-2-hydroxy-1-mesityl-3,4-dihydronaphthalene in a 92% yield (59).



A similar result was obtained with the duryl analog, the yield of product being 81%.



This type of condensation has been realized with unhindered ketones, but the yields of products are low.



REFERENCES

1. E. P. Kohler, *Am. Chem. J.* **31**, 642 (1904).
2. E. P. Kohler and E. M. Nygaard, *J. Am. Chem. Soc.* **52**, 4128 (1930).
3. J. Rigaudy, *Compt. Rend.* **226**, 1993 (1948); R. C. Fuson and H. L. Jackson, *J. Am. Chem. Soc.* **72**, 1637 (1950).
4. H. Gilman, J. E. Kirby, and C. R. Kinney, *J. Am. Chem. Soc.* **51**, 2252 (1929).
5. See K. N. Campbell and J. F. McKenna, *J. Org. Chem.* **4**, 198 (1939).
6. H. Gilman and J. Morton, *J. Am. Chem. Soc.* **70**, 2514 (1948).
7. H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.* **55**, 1265 (1933).
8. P. Pfeiffer and H. Blank, *J. Prakt. Chem.* [2] **153**, 242 (1939); H. Gilman and R. G. Jones, *J. Am. Chem. Soc.* **62**, 1243 (1940).
9. J. Schmidlin and J. Wohl, *Ber.* **43**, 1145 (1910).
10. W. A. Mosher and M. B. Huber, *J. Am. Chem. Soc.* **75**, 4604 (1953).
- 10a. P. Tomboulou and A. Metzger, private communication.
11. E. Calderaro, *Gazz. Chim. Ital.* **43** (II), 632 (1913).

12. C. F. Koelsch and R. H. Rosenwald, *J. Org. Chem.* **3**, 462 (1938).
13. C. F. Koelsch and R. H. Rosenwald, *J. Am. Chem. Soc.* **59**, 2166 (1937).
14. E. Clar, *Chem. Ber.* **65B**, 846 (1932).
15. M. Nikanishi, *Proc. Imp. Acad. (Tokyo)* **9**, 394 (1933).
16. G. Charrier and E. Ghigi, *Gazz. Chim. Ital.* **62**, 928 (1932).
17. C. F. H. Allen and S. C. Overbaugh, *J. Am. Chem. Soc.* **57**, 740 (1935).
18. C. F. H. Allen and S. C. Overbaugh, *J. Am. Chem. Soc.* **57**, 1322 (1935).
19. C. F. H. Allen and L. Gilman, *J. Am. Chem. Soc.* **58**, 937 (1936).
20. C. Dufraisse and R. Horclois, *Bull. Soc. Chim. France* [5] **3**, 1894 (1936).
21. C. F. H. Allen and A. Bell, *J. Am. Chem. Soc.* **64**, 1253 (1942).
22. C. F. Koelsch and J. A. Anthes, *J. Org. Chem.* **6**, 558 (1941).
23. T. A. Geissman and L. Morris, *J. Am. Chem. Soc.* **66**, 716 (1944).
24. V. Boekelheide and M. Goldman, *J. Org. Chem.* **19**, 575 (1954).
25. R. C. Fuson and P. Tombouljian, *J. Am. Chem. Soc.* **79**, 956 (1957).
26. W. A. Mosher and M. L. Huber, *J. Am. Chem. Soc.* **73**, 795 (1951).
27. R. C. Fuson and G. W. Griffin, *J. Am. Chem. Soc.* **79**, 1941 (1957).
28. R. C. Fuson, B. C. McKusick, and J. Mills, *J. Org. Chem.* **11**, 60 (1946).
29. R. C. Fuson, M. D. Armstrong, and S. B. Speck, *J. Org. Chem.* **7**, 297 (1942).
30. R. C. Fuson, B. C. McKusick, and F. W. Spangler, *J. Am. Chem. Soc.* **67**, 597 (1945).
31. R. C. Fuson, R. Gaertner, Y. F. Shealy, and R. J. Hellman, *J. Org. Chem.* **17**, 881 (1952).
32. R. C. Fuson and S. J. Strycker, *J. Am. Chem. Soc.* **79**, 2633 (1957).
33. P. G. Stevens, *J. Am. Chem. Soc.* **57**, 1112 (1935).
34. M. S. Kharasch and S. Weinhouse, *J. Org. Chem.* **1**, 209 (1936).
35. R. C. Fuson and R. Tull, *J. Am. Chem. Soc.* **71**, 2543 (1949).
36. R. C. Fuson and B. C. McKusick, *J. Am. Chem. Soc.* **65**, 60 (1943).
37. R. C. Fuson and F. E. Mumford, *J. Org. Chem.* **17**, 255 (1952).
38. R. C. Fuson and J. P. Freeman, *J. Am. Chem. Soc.* **76**, 911 (1954).
39. A. Bayer and V. Villiger, *Ber.* **36**, 2774 (1903).
40. P. L. Julian and W. J. Gist, *J. Am. Chem. Soc.* **57**, 2030 (1935).
41. P. L. Julian and A. Magnani, *J. Am. Chem. Soc.* **56**, 2174 (1934); P. L. Julian and W. Cole, *ibid.* **57**, 1607 (1935).
42. R. C. Fuson, R. J. Sauer, and A. Galli, unpublished work.
43. T. Severin, *Angew. Chem.* **70**, 164 (1958).
44. R. C. Fuson, E. W. Kaiser, and S. B. Speck, *J. Org. Chem.* **6**, 845 (1941).
45. A. Hoffman, M. W. Farlow, and R. C. Fuson, *J. Am. Chem. Soc.* **55**, 2000 (1933).
46. R. L. Frank and C. Weatherbee, *J. Am. Chem. Soc.* **70**, 3482 (1948).
47. R. C. Fuson and J. J. Miller, *J. Am. Chem. Soc.* **79**, 3477 (1957).
48. M. Freund, *Ber.* **37**, 4666 (1904).
49. M. Freund and G. Bode, *Ber.* **42**, 1746 (1909).
50. E. Bergman, O. Blum-Bergmann, and A. F. von Christiani, *Ann.* **483**, 80 (1930).
51. E. Bergmann and W. Rosenthal, *J. Prakt. Chem.* [2] **135**, 267 (1932).
52. H. Gilman and G. C. Gainer, *J. Am. Chem. Soc.* **69**, 877 (1947).
53. R. Gaertner, *Chem. Rev.* **45**, 493 (1949).
54. W. L. C. Veer and S. Goldschmidt, *Rec. trav. chim.* **65**, 793 (1946).
55. R. C. Fuson, H. L. Jackson, and E. W. Grieshaber, *J. Org. Chem.* **16**, 1529 (1951).
56. R. C. Fuson and L. R. Melby, *J. Am. Chem. Soc.* **75**, 5402 (1953).
57. R. C. Fuson, W. D. Emmons, and G. W. Parshall, *J. Am. Chem. Soc.* **76**, 5466 (1954).
58. P. B. Russell, *J. Am. Chem. Soc.* **74**, 2654 (1952).
59. R. C. Fuson and F. T. Fang, *J. Am. Chem. Soc.* **77**, 3781 (1955).

Infrared and Raman Spectral Studies of π Complexes Formed Between Metals and C_nH_n Rings

HEINZ P. FRITZ

*Institut für Anorganische Chemie
der Universität München
Munich, Germany*

I. Introduction	240
II. Theoretical Considerations in the Analysis of Vibrational Spectra	242
A. Principles of Molecular Spectroscopy	242
B. Interpretation of Observed Spectra	246
III. Techniques of Infrared and Raman Spectroscopy	251
A. Spectrophotometers	251
B. Preparation of Samples	252
IV. General Aspects of the Analysis of Spectra of π Complexes of Cyclic Systems, C_nH_n	254
A. Cyclic Hydrocarbons	254
B. π Complexes	255
V. Experimental Results for Three-Membered Rings	257
VI. Experimental Results for Four-Membered Rings	258
A. General Remarks	258
B. Special Cases	260
VII. Experimental Results for Five-Membered Rings	262
A. Cyclopentadienyl Anion, $(C_5H_5)^-$	262
B. Metal Cyclopentadienyls	263
VIII. Experimental Results for Six-Membered Rings	291
A. Benzene	291
B. Benzene-Metal Complexes	292
IX. Experimental Results for Seven-Membered Rings	302
A. Tropylium Cation, $(C_7H_7)^+$	302
B. π - C_7H_7 -Metal Complexes	303
X. Experimental Results for Eight-Membered Rings	304
A. Cyclooctatetraenyl Anion, $(C_8H_8)^{2-}$	305
B. π - C_8H_8 -Metal Complexes	306
XI. Some Quantities Derived from Vibrational Spectra	307
References	311
Supplementary References	315

I

INTRODUCTION

This chapter is concerned with the analysis of the vibrational spectra of organometallic compounds formed by metals and hydrocarbons of general formula $(CH)_n$. The unsaturated character of these ring systems implies the presence of highly delocalized electrons, the so-called π electrons. Most of the complexes discussed in the following pages, therefore, belong to the group of compounds called " π complexes," since the π electrons of the ligands are responsible for bond formation.

What is known today as π -complex chemistry had its origins as early as 1827 when the synthesis of a compound of ethylene, formulated as $KCl \cdot PtCl_2 \cdot C_2H_4 \cdot H_2O$, was reported by the Danish Chemist Zeise (1). Although the following century produced important results in the organometallic field, the nature of the bonding in Zeise's salt remained vague until comparatively recently. The synthesis of an unusually stable organoiron compound, dicyclopentadienyliron, $Fe(C_5H_5)_2$, by two independent groups of workers in 1951 marked the beginning of an enormous development in this area (2, 3). In rapid succession cyclopentadienyl compounds of most of the transition metals and of many main group elements became known. In addition to these results, ring systems with four, six, seven, and eight CH groups were also shown to undergo complex formation with suitable metals (4-8). Hence this chapter on the infrared and Raman spectral studies of π complexes can review compounds having $(CH)_n$ rings with $n = 4$ to 8. Of course in principle there is no reason why complexes of the cyclopropenium cation also should not exist. However no complexes of $[C_3H_3]^+$ are yet known; even the triphenyl derivative does not seem to yield complexes, although the results of some preliminary attempts are not completely clear (9-11). On the other hand, ring systems with n higher than 8 are, due to lack of planarity, less likely to form π complexes through *all* of their carbon-carbon double bonds or π electrons. However, at least in principle, even annulenes should be able to form π complexes, although not of the $Fe(C_5H_5)_2$ (ferrocene) type.

Soon after its preparation, X-ray studies established the so-called "sandwich" or "Doppelkegel" structure (12-14) for ferrocene. This structure had been proposed previously on the basis of chemical and physicochemical

evidence, including the appearance of the infrared spectrum (15). In the following years, infrared spectroscopy proved to be an invaluable tool for the preparative chemist in this field. Virtually every publication on the synthesis of new π complexes mentioned the observed infrared bands. It can be considered fortunate that efficient infrared spectrophotometers became commercially available shortly before the "renaissance" of this section of inorganic chemistry, wide application of this technique therefore becoming possible. However, many of these reports deal with the spectra in a rather qualitative way, mainly because the spectra were recorded by chemists whose chief interest was in preparative work.¹ The first thorough analyses of the vibrational spectra of complexes of the new type, $Fe(C_5H_5)_2$ and $Ru(C_5H_5)_2$, were carried out by Lippincott and co-workers (16, 17). In the course of their work Raman techniques were applied to π complexes of ring systems for the first time, although earlier Raman studies are known, e.g. for olefin compounds of silver nitrate (18).

Any exact analysis of the vibrational spectrum of a substance should be based both on infrared and on Raman measurements. Since most of the π complexes of transition metals are highly colored, the usual excitation source for Raman spectroscopy, the blue $Hg-e$ line, can be used in but few cases. However, the research of Stammreich (19) and others has provided a way for Raman spectroscopy to be used with colored substances also.

Before discussing the results it seems desirable to review briefly some of the useful techniques of infrared and Raman spectroscopy, and to give a rather elementary introduction to the analysis of vibrational spectra. Since this series of volumes is intended for readers who may not be thoroughly conversant with group theory, a nonmathematical discussion of a few rules which can be used to determine the numbers and types of vibrations to be expected for a given molecule is also given.

The literature coverage is as complete as possible up to the end of 1962. Publications such as "Current Chemical Papers" and "Chemical Abstracts" have been scanned for references up to the middle of 1963. One finds but few spectra of π complexes in commercial spectra catalogs and practically no mention of them in reviews, such as those of Bellamy (20) or Lecomte (21). However, a short survey of the infrared spectra of cyclopentadienylmetal complexes appeared in 1960 (22).

¹ In this chapter no papers concerning mainly the preparation of complexes will be referred to.

II

THEORETICAL CONSIDERATIONS IN THE ANALYSIS OF
VIBRATIONAL SPECTRA*A. Principles of Molecular Spectroscopy*

Molecular spectroscopy, especially as it concerns organometallic compounds, deals mostly with the normal frequencies of the molecules, i.e. with those frequencies which are absorbed or emitted when all atoms of a molecule vibrate in an approximately harmonic motion and in the same phase.

The normal frequencies are the observed result of normal vibrations (hereinafter abbreviated n.v. in this chapter) corresponding to transitions from the vibrational ground state to the first excited one, and are usually observed at room temperature. Generally the selection rule $\Delta\nu = \pm 1$ is obeyed. By infrared radiation rotational motions of the molecules are also excited. Their absorptions are superimposed on those of the vibrational modes. However, no example is known where rotational fine structure has been resolved for a π complex.

The number of normal frequencies depends on the number of atoms or, more accurately, on the number of parameters of the covalent bonds connecting the atoms in a compound. For an N -atomic molecule it is $3N - 5$ for a linear and $3N - 6$ for a nonlinear structure. Such a normal frequency is infrared-active, and so can be expected to appear in the IR spectrum, when it results from a periodic change of a dipole moment existing in the molecule or at least in the particular bond concerned. The intensity of a band is proportional to the square of the transition moment. The vibration of a more polar bond such as C—O, therefore, will have a higher intensity than that of a less polar bond such as C—C.

When exciting radiation is incident upon a molecule, the alternating field may induce a dipole moment in the molecule. If the vibration produces a change in this induced moment, the normal frequencies will also be observed in the Raman spectrum. Thus, the Raman effect is associated with changes in the polarizability of the molecule. The radiation emitted is mostly of the same frequency as the exciting radiation (Rayleigh scattering). The molecular vibrational frequencies, ν , are superimposed on this scattering effect with greatly reduced intensities. There are two series of Raman lines, $\nu_0 \pm \nu$, symmetrical to the exciting line ν_0 which are called Stokes and anti-Stokes lines, respectively. The Stokes lines are usually used for Raman spectroscopy

since they appear with higher intensity. This intensity is proportional to $(\nu_0 - \nu)^4$.

A spectrum thus represents a series of frequencies corresponding to infrared absorptions or to Raman shifts, expressed in cm^{-1} or wave numbers. The position of the various frequencies is in the main determined by two factors:

- (a) the masses of the vibrating atoms of a bond;
- (b) the type and strength of the bonding forces between the atoms.

The higher the frequencies appear the smaller the masses must be and the stronger are the bonds. Therefore, for a certain combination of atoms, e.g. $\text{C}=\text{O}$ in carbonyl compounds, frequency and bond order are proportional, to a good approximation, and the frequencies appear in the same spectral range for a particular group in different molecules. In this event a so-called "group frequency" can be assigned (cf. ref 20).

Another criterion for the position of a frequency is the type of vibration causing this frequency. Vibrations can be classified according to the type of movement of the atoms. During "stretching" or "valence" vibrations mainly bond lengths alter, and during "deformation" vibrations bond angles change. However, a clear-cut division of these two different types of vibrational modes is impossible, since normally each vibration appears as a mixture of "pure" (but in a strict sense hypothetical) vibrational modes. This can be seen clearly in a mathematical treatment since in these cases off-diagonal elements appear in the secular equation describing the system. Nevertheless, while keeping in mind that the approach is not exact, vibrations normally can, to a good approximation, be treated either as stretching or deforming, according to their predominant character.

In π complexes of C_nH_n rings the molecule will have an especially large number of symmetry elements, for example mirror planes [σ], rotation axes [C], centers of symmetry [i], etc. In such cases, the normal vibrations also have these symmetry properties. Based on the results of group theory the symmetry behavior of normal vibrations can be arranged in so-called "character tables." These have been determined for all the more common symmetry groups (23–27). These symmetry groups are those used in crystallography, with the addition of groups with fivefold, sevenfold, etc. symmetry axes.

The conventional way of writing such a table is illustrated by that for the C_{3v} group of the trigonal pyramid (e.g. NH_3), Table I. In the first row the

symbols of the symmetry operations of the symmetry group are listed, beginning with the group symbol C_{3v} , followed by the identity operation E or I , the two rotations about the threefold z -axis (C_3), and reflection at the three vertical mirror planes going through C_3 (σ_v). The first column gives the symbols of the so-called "irreducible representations"² of the symmetry group. The other columns indicate the variation of the coordinates of a n.v. under the corresponding symmetry operation stated at the top of each column. Thus, for example, $+1$ or -1 means that by using the symmetry operation concerned, a n.v. is left unchanged or reverses its sign. These cases are referred to as symmetric and anti- or asymmetric symmetry behavior (23–26).

TABLE I
CHARACTER TABLE FOR POINT GROUP C_{3v}

C_{3v}	$E(I)$	$2C_3(z)$	$3\sigma_v$
A_1	$+1$	$+1$	$+1$
A_2	$+1$	$+1$	-1
E	$+2$	-1	0

Normal vibrations being symmetric with respect to all symmetry operations of a point group—in our example, belonging to the A_1 representation—are called totally symmetric. This is an important property especially for Raman spectroscopy since these n.v. always occur in Raman spectra and usually with high intensity. Symmetry operations are identified by the symmetry element "generating" them. Indices usually give a more precise definition of each symmetry element. Thus, while the symbol σ indicates a mirror plane in general, σ_h 's are all such planes lying horizontally to a principal axis of symmetry (e.g. the plane of the six carbon atoms of benzene); σ_v 's are vertical planes containing the axis of highest symmetry (C_6 of benzene); and σ_d 's are mirror planes "diagonally" bisecting the angles between σ_v 's (Fig. 1). Rotations are classified by the number of "steps"

² Irreducible representation is the group theory term for a certain combination of symmetry properties of wave functions, normal vibrations, etc., which cannot be simplified (reduced) further by a transformation. The whole of the irreducible representation describes the symmetry or point group.

which lead to assumption of the original position. This number is added as subscript to the general symbol C of a rotational axis. For example, a three-fold rotation axis (C_3) will place the atoms of a molecule in identical positions by rotations of 120° and to the original position in three successive rotations of 120° each. Therefore, the angle of rotation is $(2\pi/n)^\circ$. Since all the symmetry operations of one type, for example all rotations of 120° , form a subgroup of the entire symmetry group they have the same characters. Hence, in the character table of C_{3v} we have $2C_3$ and $3\sigma_v$ each heading one

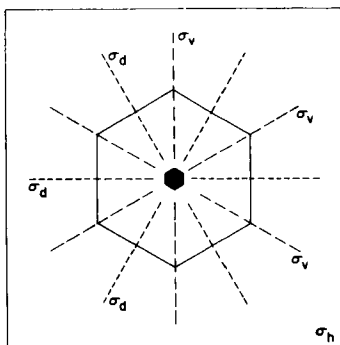


FIG. 1. Mirror planes of benzene.

column. Thus the number in front of the symbol of the symmetry operations indicates how many of them are possible.

Symmetry groups are usually designated by combinations of symbols according to Schönflies. Thus, C_{3v} indicates the presence of a C_3 axis and of three σ_v 's in a molecule. Point groups, which have n twofold axes of symmetry perpendicular to the n -fold axis are designated by D_n . If a horizontal plane of symmetry is present also, this leads to groups D_{nh} . This is important in discussing planar rings of the C_nH_n type.

The following symbols are used for distinguishing the irreducible representations of a character table:

- A and B Irreducible representations which are symmetric or asymmetric respectively, referred to a particular n -fold symmetry axis, C_n , usually the axis of highest n .
- $E, F, G \dots$ 2-, 3-, and 4-fold degenerate irreducible representations. It should be noted that in ligand field theory the triply degenerate states are usually represented by T , and not by F .

1 and 2	Irreducible representations respectively symmetric or asymmetric referred to "nondistinguished" axes or indices (symmetry elements).
+ and -	Irreducible representations respectively symmetric or asymmetric with respect to twofold axes, C_2 .
g and u	Irreducible representations respectively symmetric or asymmetric with respect to a center of symmetry (inversion), i .
' and "	Irreducible representations respectively symmetric or asymmetric with reference to a horizontal mirror plane, σ_h .

Some of these symbols include degenerate irreducible representations. This means that two, three, or more vibrations are of the same energy and have the same frequency. For example twofold degeneracy can result when two vibrations are orthogonal, i.e. when their amplitudes are at an angle of 90° to each other and of the same size.

The reader is strongly recommended at this point to refer to the literature to obtain a more thorough knowledge of the above material (23-26, 28). The mathematical treatment of vibrating systems cannot be given in the brief space available here. Furthermore, such treatment lies beyond the usual needs of most chemists. On the other hand, with regard to an understanding of modern theory of complex bonding (ligand field theory) or the concept of electronic "shells," every modern inorganic chemist should be acquainted with the importance of symmetry considerations.

B. Interpretation of Observed Spectra

The interpretation of an observed vibrational spectrum can be carried out with various objects in view:

1. Simple comparison of the spectrum of a compound with those of others can prove the identity with, or the near relationship to, already known compounds.
2. By means of characteristic group frequencies, e.g. of $C=O$, CH_3-C , or C_6H_5 groups, suggestions as to the constitution of unknown compounds can be made.
3. Shifts of known frequencies can be used to understand changes in bonding in compounds of similar constitution.
4. The integrated intensities of certain bands give bond moments, providing evidence concerning bond types and forces.

5. From the stretching frequencies and the masses of the vibrating atoms, the force constants of the corresponding bonds can be determined.
6. Vapor phase measurements of relatively simple molecules can lead to determination of interatomic distances from rotational structures of bands.
7. Spectroscopic predictions and selection rules can be compared with the observed spectrum. On this basis, the molecular symmetry of the molecule can often be determined.
8. Based on an analysis of the vibrational spectrum, thermodynamic data can be calculated.

While the first three points list the procedures normally applied by the preparative chemist, the later ones suggest procedures which can be used to gain a more thorough understanding of the compounds involved. In the following pages these objectives will be applied to the discussion of the spectra of π complexes. Of course, there are other more specialized techniques which utilize spectroscopic studies as well, e.g. kinetic work.

1. *Procedure for Spectral Analysis*

We shall not be concerned here with the exact treatment of spectra by "normal coordinate analysis" (24, 29). Instead an attempt will be made to give some semiempirical rules, which will enable us to predict the correct number and types of vibrations in the infrared or Raman spectrum for a given symmetry. If the observed spectrum coincides with theoretical expectations, we can be reasonably sure that we predicted the correct symmetry. However, we cannot be absolutely certain, since one can never be sure that the number of frequencies found is not too low (or more seldom too high) for an assumed symmetry. It is not so much the correct application of the rules, but rather the interpretation of the experimental findings that is decisive. It is, therefore, in most cases involving hydrocarbon complexes, advisable and sometimes necessary to obtain additional evidence from measurements on deuterated compounds, from comparisons of the spectra of similar compounds, or from considerations of chemical facts, in order to make sure that the determination of a symmetry group is well-founded.

If a structural problem can be reduced to the determination of symmetry, the structure of the compound can usually be established. One can at least exclude possible structures whose predicted frequencies do not agree with those observed. The term "symmetry" must be applied in this context with

some reservation, since there are distortions of the equilibrium symmetry during some of the normal vibrations.

2. Rules

Before discussing a few rules for predicting some properties of the vibrational spectra, we must introduce additional terminology both for better understanding and for convenience.

Stretching vibrations can be indicated, following Kohlrausch (25), by ν for a C—H stretch and by ω for a stretching mode of a skeletal bond, mostly C—C in the complexes of ring systems C_nH_n here discussed. Deformation modes sometimes are classified by terms such as “wagging,” “rocking,” “scissoring,” etc. We shall restrict our terminology to two terms, indicating (if possible) the main direction of the deformational vibration with respect to a particular symmetry element in the molecule. Therefore, for planar ring systems C_nH_n there are in-plane (or parallel) deformations δ (for —C—H) and Δ (for C—C—C), as well as out-of-plane (perpendicular) deformations, γ (for —C—H) and Γ (for C—C—C—C).

The well-known $3N - 6$ or $3N - 5$ rules for compounds with N atoms can be presented in a simple way. In a molecule, there will be as many stretching vibrations as there are bonds. Since two atoms are needed for one bond, three for two bonds, etc., this gives a rise to a total of $N - 1$ stretching modes (ν, ω). For a parallel deformation at least three atoms are needed, so that in general there are $N - 2$ vibrations of this type. Similarly, $N - 3$ is the number of perpendicular deformations. However, the approximate nature of the description of vibrations should always be borne in mind. If there is one closed ring in a molecule, one of the δ modes changes to a (predominantly) stretching mode. This principle continues to act for each new additional ring closure in the compound. If the new ring is in the same plane as the original ones, a Δ vibration changes to an ω ; if it is joined at an angle to the original ones, a Γ becomes a stretching mode. This rule, however, does not apply for π complexes, where one could assume many rings to be formed by the central metal with each pair of neighboring C atoms of the ring ligands.

From consideration of the character tables associated with various point groups, one can easily find the number of n.v. belonging to the different irreducible representations of any particular symmetry group. The procedure for accomplishing this is discussed lucidly by Herzberg (24), so explanation can be omitted here. Moreover, the way to find the irreducible representations of a point group, the n.v. of which are infrared- or Raman-

active, has also been described by Herzberg. The most common cases have been tabulated elsewhere (24, 27).

One of the important rules in this context is the "rule of mutual exclusion" (30) which states, that in a molecule possessing a center of symmetry, all n.v. asymmetric to this center of symmetry are Raman-inactive and all vibrations symmetric to it are IR-inactive.

Even if we know the number of normal frequencies of each of the different types to be expected for a molecule and also how many of them must belong to each of the various irreducible representations of the point group and hence how many of them must appear in the IR or Raman spectra, the important question of which n.v. appear in which irreducible representation must still be answered. If we can draw pictures of all the possible n.v. this is not very difficult. One must only observe how the coordinates change under a certain symmetry operation. When this is done for all symmetry operations of the point group, the symmetry behavior and the irreducible representation can be established. This procedure becomes more difficult as the structure of the molecules being considered becomes more complicated.

We shall now show how to proceed to assign stretching vibrations to the different irreducible representations. For the deformation modes there is in principle no difference, and the application of this procedure to examples of interest to the reader can be easily carried out, if the symmetry properties of the deformations are checked against the character tables.

As a first step it is advisable to classify all atoms of a molecule in "equivalent sets." Such a set includes all nuclei, which "go over into themselves" by a symmetry operation. In the benzene molecule, for example, there are two equivalent sets—considering all the C atoms and all the H atoms—since they can be brought into identical position by rotation around the sixfold axis of symmetry. The lower the symmetry is, the more equivalent sets of atoms must be present in a molecule and the fewer irreducible representations belong to the point group. In general, every equivalent set or every bond between equivalent sets can contribute no more than one stretching vibration to each representation.

Starting from the equilibrium symmetry of the molecule we next must determine on which symmetry elements the amplitudes (or elongations) of the stretching vibrations lie. If they lie on any symmetry elements at all, then the "sets of amplitudes" do not contribute stretching modes to those irreducible representations of the point group which are asymmetric with respect to these symmetry elements. Obviously, planes of symmetry should

be considered first, since axes can be regarded as intersecting lines of two or more planes. Also axes C_n with odd indices exhibit symmetry behavior that is a little more complicated in the general case (31).

As an empirical rule, we shall consider the σ_v or σ_d , depending on how essential they are for the bond whose stretching modes we wish to describe. For example, for the C—H bonds in benzene the σ_v 's should be used, and for the C—C bonds the σ_d 's. In addition, the σ_h 's must be considered for all groups for which the rule of mutual exclusion is valid. Similarly, D_{5h} or D_{7h} must also be treated this way even though they do not have a center of symmetry. In all irreducible representations where the Tables show as character in the column of the above-mentioned symmetry planes a +1 for nondegenerate and a +2, +1, or 0 for degenerate vibrations, stretching modes will appear. It is thus possible to predict stretching modes for the C—H bonds in benzene of type A_{1g} , B_{1u} , E_{1u} , and E_{2g} , for C—C bonds of type A_{1g} , B_{2u} , E_{1u} , and E_{2g} . Stretching modes for the C—O bonds in $\text{Cr}(\text{CO})_6$ are of type A_{1g} , E_g , and F_{1u} . In all these examples, when the degeneracies are considered there are six stretching modes. These predictions have, in all cases, been confirmed experimentally.

On the basis of the principles discussed earlier, it is possible to predict which vibrations will occur in the infrared or in the Raman spectra. Hence we find that in the two examples C_6H_6 and $\text{Cr}(\text{CO})_6$ there will be only one stretching mode E_{1u} and F_{1u} respectively in the infrared, and two stretching modes each in the Raman spectrum, A_{1g} and E_{2g} , and A_{1g} and E_g respectively.

An additional example will be given to illustrate further the use of this empirical method. For $\text{Co}_2(\text{CO})_8$ seven CO stretching vibrations have been observed (32, 33), and C_{2v} symmetry was assigned to the molecule. The structure as established by X-ray diffraction (34) is that of two octahedra interconnected at a face. Two bridging carbonyls occupy corners of the "bonding triangle." Three corners of each octahedron hold terminal CO groups, the Co atoms are located in the centers of the octahedra. Thus, there are four terminal CO's forming an equivalent set on no symmetry element. Hence, in each of the four irreducible representations one stretching mode of this set of four groups will appear. Two other terminal CO groups (at apices of the octahedra) form another set in what can be called the yz -plane. Therefore, these CO groups contribute one stretching mode to A_1 and B_2 . Finally, the bridging CO groups can stretch in the xz -plane and therefore have modes in A_1 and B_1 . Since only the representation A_2 is infrared-inactive, there remain seven IR-active bands corresponding to C_{2v} .

In order to obtain the Co—C stretching vibrations it is only necessary to treat the CO group as a unit: this is equivalent to simply ignoring the oxygen atoms. If this is done, the molecule can be considered to be a ten-atom entity. Application of the rules leads to seven Co—C stretches which are IR-active in the same irreducible representation, as for the C—O case. Finally, ignoring also the eight C atoms, one remaining stretching vibration for Co—Co is found. This, ω_{CoCo} , represents the stretching of a Co—C—Co ring after ring closure. Altogether there are $8 + 8 + 1 = 17$ stretching vibrations for $Co_2(CO)_8$, in agreement with the $N - 1$ rule.

Another possible “nonmathematical” treatment of the problem of obtaining the correct assignment for n.v. is that of starting from a known “parent compound” and tracing the correlations when changing from one (preferably higher) symmetry group to another. Thus in the case of a trigonally distorted benzene one can start from the well-known frequency assignments for C_6H_6 in D_{6h} and go over to D_{3h} . Since in D_{3h} , A_2' and E' are infrared-active, and A_1' , E' , and E'' are Raman-active, all vibrations of the normal benzene belonging to representations which go over into one of these irreducible representations of D_{3h} will be observable. These benzene representations are A_{2u} , B_{2u} , E_{1u} , and E_{2g} in the IR, and A_{1g} , B_{1u} , E_{1g} , E_{1u} , E_{2g} , and E_{2u} in the Raman. It can be seen that usually more modes are active in the Raman spectrum than in the IR spectrum.

III

TECHNIQUES OF INFRARED AND RAMAN SPECTROSCOPY

A. Spectrophotometers

There are no special requirements regarding the spectrophotometers needed for infrared work on π complexes. The increasing use of grating instruments will bring about some improvement, particularly concerning resolution and access to the far-infrared region. However, almost all data reported in this chapter were obtained with prism spectrophotometers using the well-known LiF, NaCl, CaF_2 , KBr, CsBr, or CsI optics. There is ample literature available concerning infrared instrumentation (21, 27, 35).

In Raman studies with prism (17, 36) or grating instruments (19) the strong $Hg - e$ (4358 Å) line has seldom been used for excitation of Raman scattering, due to the sensitivity of most complexes to intense high energy

light and also to their strong absorption in the visible spectral range. These difficulties can in some cases be overcome by exciting with lines of Hg— c (5461 Å), Na (5839 Å), He (5875.6, 6678.2, and 7281.4 Å) (19), or other rare gases, using discharge tubes filled with the corresponding vapor or gases. Detailed descriptions of Raman techniques are available in the literature (19, 28, 37).

B. Preparation of Samples

Descriptions of the preparation of samples for normal infrared (22, 27) or Raman work (28) can be readily found, and differences between the various methods have been discussed (22). However, in preparing most of the transition metal π complexes for spectroscopic investigations, additional difficulties are sometimes encountered. These difficulties arise from the characteristic properties of these substances.

1. Vapor Phase Measurements

As is commonly known, spectra obtained from molecules in the gas phase are the most useful, since all theoretical conclusions are based principally on the assumption that the molecules are not influenced by any outside forces. However, only a few vapor phase studies of complexes of C_nH_n ring systems with metals have been reported. In one instance (17) a conventional 1-meter gas cell was used at a temperature of about 110° C, and in another instance (38) a 9-cm cell was used up to 210° C. Most of the complexes have a rather low vapor pressure at room temperature, so that elevated temperatures must be used. However, complexes described as stable up to temperatures considerably higher than those used for the infrared measurements often show strong decomposition. Hence the observed spectra of the π complexes in the gas phase have superimposed on them the spectra of the decomposition products. Moreover when higher temperatures are employed, it is almost always necessary to provide some auxiliary means of heating the cell windows, for the complexes show a marked tendency to sublime onto the cool window surface. An all-glass cell for the investigation of C—H stretching frequencies has been described (39). Another difficulty lies in the possibility of photodecomposition. This apparently can occur even with infrared light (or light from the Nernst glower) when the complex is in the vapor phase at elevated temperatures. Naturally with air-sensitive compounds care must be taken to exclude oxygen. A glove box can be used to fill the cells. A

possible difficulty here is that a rather large inert gas lock is required to hold the heatable cell.

Other possible techniques are sublimation of the sample into the cell attached to a vacuum system, or the insertion of the samples in small glass ampoules which are cracked after the cell is filled with pure inert gas.

2. *Liquid or Dissolved Phase Measurements*

Even if the solid complex is stable in air, measurements on solutions can involve difficulties which arise from the solvent. For example, halogenated hydrocarbons (perhaps due to impurities of free halogen or hydrogen halides) often cause decomposition of the compounds dissolved in them. Photodecomposition of the complex during Raman work can also be extensive, for example, even $(C_5H_5)_2Os$, a colorless, air-stable complex is decomposed in carbon tetrachloride solution by $Hg-e$ irradiation. Furthermore it is often found that complexes are much more sensitive to oxygen when they are in solution than when they are solids, probably because of the high degree of dispersion in solution. Therefore, it is best to use only solvents carefully purified from traces of oxygen. By this procedure the solvents are also freed from moisture, which decomposes quite a number of π complexes.

The safest method for filling cells for liquid phase infrared and Raman measurements is to place the solid sample in the cell (e.g. by sublimation), and then to distill the solvent into the cell. Both operations should be carried out with the cell attached to a vacuum system. A quicker procedure, but sometimes not as satisfactory, involves filling the cells in a glove box. Traces of oxygen can be effectively excluded by flushing the glove box thoroughly by purified nitrogen and then filling it with a heavier gas such as argon.

Solvents or compounds which attack the alkali-halide windows can be handled in normal cells by lining the cell with a very thin sheet (*ca.* 0.05 mm) of Teflon or polyethylene.

3. *Solid State Measurements*

For obtaining Nujol, Fluorolube, hexachlorobutadiene, etc., mulls of polycrystalline samples under inert gas protection, one can once again use glove boxes. Very often, however, it is more convenient to handle the compounds in small Schlenk tubes. In these tubes manual or vibratory grinding of the substance can be carried out in a current of inert gas. Usually even moderately air-sensitive complexes can be placed between the cell windows in air if the substance is emulgated with Nujol or Fluorolube.

It is possible to provide some nitrogen protection also when KBr or CsBr disks of polycrystalline samples are to be made. However, except where the entire press can be operated under nitrogen, only the less air-sensitive compounds can normally be examined as halide disks. The Schlenk tube technique may also be employed for handling these substances and the medium (e.g. KBr, etc.).

It is sometimes advantageous to sublime or crystallize the complex directly onto a halide window. However, oriented crystal growing can effect the intensity ratio of the various bands. Indeed single-crystal studies rely on these effects. The only investigation of this type which has been reported was carried out on ferrocene (40). However, an attempt has been made to obtain infrared spectra of the dicyclopentadienyls of Fe, Mg, and Mn as single crystals sealed between AgCl windows (41).

IV

GENERAL ASPECTS OF THE ANALYSIS OF SPECTRA OF π COMPLEXES OF CYCLIC SYSTEMS, C_nH_n

A. Cyclic Hydrocarbons

The non-complex bonded cyclic systems C_nH_n possess symmetry groups D_{nh} , provided they have a planar, regular polygonal structure. The bands belonging to the irreducible representations listed in Table II are infrared and Raman-active as shown.

TABLE II
IRREDUCIBLE REPRESENTATIONS AND NUMBERS OF IR- AND RAMAN-ACTIVE NORMAL
VIBRATIONS OF CYCLIC D_{nh} SYSTEMS

D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}
<i>IR-active</i>					
$A_2'' \left. \vphantom{\begin{matrix} A_2'' \\ E' \end{matrix}} \right\} 4$	$A_{2u} \left. \vphantom{\begin{matrix} A_{2u} \\ E_u \end{matrix}} \right\} 4$	$A_2'' \left. \vphantom{\begin{matrix} A_2'' \\ E_1' \end{matrix}} \right\} 4$	$A_{2u} \left. \vphantom{\begin{matrix} A_{2u} \\ E_{1u} \end{matrix}} \right\} 4$	$A_2'' \left. \vphantom{\begin{matrix} A_2'' \\ E_1' \end{matrix}} \right\} 4$	$A_{2u} \left. \vphantom{\begin{matrix} A_{2u} \\ E_{1u} \end{matrix}} \right\} 4$
<i>Raman-active</i>					
$A_1' \left. \vphantom{\begin{matrix} A_1' \\ E' \\ E'' \end{matrix}} \right\} 6$	$A_{1g} \left. \vphantom{\begin{matrix} A_{1g} \\ B_{1g} \\ B_{2g} \\ E_g \end{matrix}} \right\} 7$	$A_1' \left. \vphantom{\begin{matrix} A_1' \\ E_1'' \\ E_2' \end{matrix}} \right\} 7$	$A_{1g} \left. \vphantom{\begin{matrix} A_{1g} \\ E_{1g} \\ E_{2g} \end{matrix}} \right\} 7$	$A_1' \left. \vphantom{\begin{matrix} A_1' \\ E_1'' \\ E_2' \end{matrix}} \right\} 7$	$A_{1g} \left. \vphantom{\begin{matrix} A_{1g} \\ E_{1g} \\ E_{2g} \\ E_{3g} \end{matrix}} \right\} 7$

It can be seen that for C_nH_n systems with $n > 4$ regardless of the size of the ring four infrared-active normal vibrations and seven Raman-active ones are to be expected. Since the members of the series with $n = 3$ and 4 are known only with phenyl substituents or in complexes, it is impossible to observe their n.v. unaffected by conjugation or complex bonding effects. However, for the higher members, it suffices for establishing structures to find spectra with only a few bands, namely the four IR- and seven Raman-active ones. In addition, Table II shows that the rule of mutual exclusion is strictly valid, although D_{5h} and D_{7h} do not have a center of inversion.

B. π Complexes

As will be seen from the following discussion of the different types of complexes formed by C_nH_n (especially from the treatment of the cyclopentadienyls), we can distinguish in a formal way between the frequencies of vibrations of the ligands themselves and those of the "framework" (or "skeleton") of the complex when the ligand rings are assumed to be rigid disks. In doing this we are following a procedure used earlier by Crawford and Wilson for methyl compounds. Thus, for example, the spectrum of neopentane, $C(CH_3)_4$, can be explained as a combination of the partial spectrum of a CH_3 group (local symmetry C_{3v}) and that of the carbon skeleton (symmetry T_d) (42). Another example, this time from inorganic chemistry, is $[Cr_2O_7]^{2-}$ (43), the spectrum of which is the superposition of the partial spectra of a CrO_3 group and of the $Cr-O-Cr$ system, respectively. This method of "local symmetry" was applied for the first time to π complexes by Cotton (22).

Essential for treating the linear, plane trigonal, or tetrahedral "Mehrkessel" (many cone) molecules is the fact that the metal-ligand group having C_{nv} symmetry and the $YXY-$, XY_3- , or XY_4- structures of the skeleton can couple through their A_1 vibrations, since they have vector components along the molecular axes and hence coupling terms of the potential energy.

In the following discussion therefore a distinction is usually made between spectra of the ligands, and spectra or frequencies of the molecular framework.

Two extreme cases can be considered illustrating two different ways of looking at spectra. These two cases are distinguishable by the strength of the coupling between the vibrations of the two ligands which exists, or can be assumed to occur, through the central atom. In the case of a sandwich

molecule like ferrocene this involves coupling between the rings. In the presence of substantial coupling, the selection rules of the symmetry groups have to be applied to the entire molecule. Even if results from other measurements are considered, for example, the establishment of a center of symmetry in the molecule by X-ray diffraction, the structure of the single ligand cannot be established unambiguously. In the case of no coupling or relatively unimportant coupling the vibrational spectrum can be regarded as the superposition of the partial spectra of one ligand with that of a "pseudo-three-mass" model (ring-metal-ring). Then the ligand ring spectra of the complexes must be compared as perturbed D_{nh} rings, which while retaining their n -fold symmetry have a "forced" lowering of symmetry by complex bonding to a C_{nv} local symmetry. Table III compares the number of ligand vibrations for dibenzene-metal complexes in these two cases for some important possible structures, degenerate vibrations being counted only once.

TABLE III
NUMBER OF LIGAND VIBRATIONS IN DIBENZENE-METAL COMPLEXES OF DIFFERENT SYMMETRIES

	Symmetries				
	Strong coupling			Weak coupling	
	D_{3d}	D_{6h}	D_{6d}	C_{3v}	C_{6v}
IR-active n.v.	17	7	7	17	7
Raman-active n.v.	17	13	13	20	13
Completely inactive n.v.	6	20	14	0	7

Thus both approaches lead to the same numbers of frequencies for all the six fold symmetry groups in both the infrared and Raman spectra, and thus a distinction between the two approaches is impossible. The same is true for the threefold symmetries in the infrared, and almost so in the Raman spectrum. It can be shown that this result can be generalized for all ring systems C_nH_n , since not only the number but also the types of vibrations are the same in every case. Especially in the case of cyclopentadienyl complexes it can be seen that the tri- and tetracyclopentadienyls exhibit ligand spectra

which correspond closely to those of the mono- and dicyclopentadienyls. The total symmetry of such a complex can be determined except for the establishment of the existence of a center of symmetry. For example, an analysis of the vibrational spectrum of ferrocene, $Fe(C_5H_5)_2$, reveals that the molecule has either D_{5d} or D_{5h} symmetry, but does not make possible a decision between these two alternatives.

We can thus conclude that the consideration of the spectra of predominantly covalent complexes as composed of C_{nv} ligand and skeleton frequencies (weak coupling case) is a meaningful and illustrative approach to the problem. The "strong coupling" case is more exact, but less informative. It must be remembered of course that the transition from strong to weak coupling can be determined only empirically. Both methods have been applied to the spectra of complexes, the first to ferrocene (17) and dibenzenechromium cation (38), and the second, for example, to benzenechromium tricarbonyl (44).

Regardless of the approach taken, the method for obtaining the number of vibrations for sandwich compounds is the same. This can be illustrated for ferrocene, $Fe(C_5H_5)_2$. Altogether the molecule has 21 atoms; therefore, $3N - 6 = [3(21) - 6] = 57$ normal vibrations are to be expected. Each C_5H_5 ligand has $[(3 \times 10) - 6] = 24$ ligand vibrations. There are two ligands, so the total number of ligand vibrations is 2×24 , or 48. Thus the remaining $(57 - 48) = 9$ n.v. are framework, skeleton, or "inner" vibrations.

V

EXPERIMENTAL RESULTS FOR THREE-MEMBERED RINGS

In Hückel's $(4n + 2)$ series, the cyclopropenium cation $(C_3H_3)^+$, now known in the form of phenyl-substituted derivatives (45), is the first member. All attempts to obtain π complexes of this aromatic system have so far been unsuccessful. Cyclopropenyl halides have been treated with $[Co(CO)_4]^-$ and $[Fe(CO)_3NO]^-$ (9), with $PdCl_2$ and $Ni(CO)_4$ in various solvents (10), and with $K[PtCl_3 \cdot C_2H_4]$ (11) without success. Only compounds which probably have a CO group incorporated in the ring ligand in some not yet identified way, or saltlike compounds were isolated. An attempt was made to enter the cyclopropenium series starting from cyclopropene derivatives but again no really pure compounds or satisfying results

could be obtained (10). Therefore, spectroscopic studies have to be restricted for the time being to the free cations. There can be little doubt, however, that the synthesis of π complexes of the C_3 system is just a matter of finding a suitable reaction path.

Since the presence of phenyl substituents always complicates the analysis of vibrational spectra of ring systems C_nH_m , a detailed interpretation of the spectra of cyclopropenium cations must in these cases also be incomplete. Subtracting the 27 normal vibrations of one C_6H_5 group, then for the C_3 ring only one infrared-active normal vibration is to be expected; this can be tentatively assigned at 1414 cm^{-1} by comparison with the spectra of diphenylacetylene or hexaphenylbenzene. This frequency corresponds to the n.v. of benzene at 1485 cm^{-1} , i.e. a ring vibration, which involves C—C stretching and ring deformation modes. This intense band is not found in cyclopropene derivatives. Their C=C-stretching modes appear at extremely high frequencies (46), in diphenylcyclopropenone even at 1850 cm^{-1} (47). The high electron density of the three-membered ring, which shows up clearly for cyclopropane (48), makes this unusual frequency understandable.

VI

EXPERIMENTAL RESULTS FOR FOUR-MEMBERED RINGS

A. General Remarks

The cyclic system cyclobutadiene (C_4H_4) has been sought for almost half a century. Recently π complexes of the cyclobutadiene system C_4X_4 , with $X = H, CH_3$, or C_6H_5 , have been reported. Thus diphenylacetylene and $Fe(CO)_5$ react to form, among several other complexes, yellow $C_4(C_6H_5)_4Fe(CO)_3$. The syntheses of purple $C_4(CH_3)_4NiCl_2$ and colorless " $C_4H_4AgNO_3$ " followed. More recently, dark red-brown $C_4(C_6H_5)_4PdCl_2$, dark blue $C_4(C_6H_5)_4NiCl_2$ and $C_4(C_6H_5)_4NiBr_2$, and red-brown $C_4(C_6H_5)_4CoC_5H_5$ have been obtained.

X-ray studies of the first two complexes established the existence of a square planar carbon ring in the C_4 group with the substituents turned slightly out of the ring plane (49, 50). The central atom and the metal-organic part of the complexes have the C_{4v} symmetry of a tetragonal pyramid. The spectra of the ligands must be in accord with this symmetry. Considering

the substituents as points of mass X , we obtain the picture shown in Fig. 2. Application of the rules mentioned above (Section II) leads one to expect bands of the number, types, and activities given in Table IV. In this and succeeding tables, the type of vibration is given in brackets [], and the numbers of the assigned n.v. (see Table VI) are given in parentheses (). In the column headed "Activity," the symbols p, dp, and fb refer to the Raman effect, and indicate vibrations which are polarized, depolarized, and forbidden, respectively. The letters ia denote frequencies inactive in the

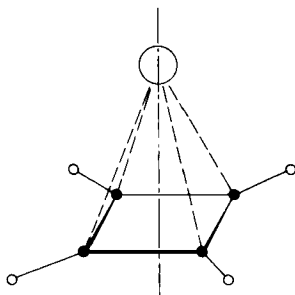


FIG. 2. Structure for cyclobutadiene complexes.

infrared. Infrared-active vibrations are designated by M_z or M_{xy} , the subscripts indicating the direction of the changing components of the dipole moment for these vibrations. Besides the metal-ligand stretching (A_1) and the metal-ligand-deformation vibrations (E), there are seven infrared-active n.v., five of which are movements of the substituents against the C_4 ring and two of which correspond to inner vibrations of this ring. Again, because of the many bands due to the phenyl groups, the IR spectra of all the phenyl-substituted derivatives could be treated only rather tentatively (51).

TABLE IV
SPECTRAL EXPECTATIONS FOR $M-C_4X_4$ WITH C_{4v} SYMMETRY

C_{4v}	$M-C_4X_4$	C_4X_4	C_4	$C-X$	$M-Ligand$	Activity
A_1	4	3	1 [ω] (1)	2 [ν, γ] (2, 3)	1 [ω] (4)	p, M_z
A_2	1	1	—	1 [δ]	—	fb, ia
B_1	4	4	2 [ω, I']	2 [ν, γ]	—	dp, ia
B_2	2	2	1 [Δ]	1 [δ]	—	dp, ia
E	5	4	1 [ω] (5)	3 [ν, δ, γ] (6, 7, 8)	1 [I'] (9)	dp, M_{xy}

B. Special Cases

1. $\pi\text{-C}_4(\text{CH}_3)_4\text{NiCl}_2$

The first characteristic bands of this complex were listed at the time of the report of the synthesis. Once the infrared spectrum had been obtained, an attempt could be made to apply our knowledge of local symmetries.

TABLE V
SPECTRAL EXPECTATIONS FOR C—CH_3 GROUPS WITH SYMMETRY C_{3v}

C_{3v}	C—CH_3	$\text{C—(CH}_3)$	—CH_3	Activity
A_1	3	1 [ω] (2)	2 [ν , γ] (10, 11)	p, M_z
A_2	—	—	—	dp, i_a
E	3	1 [rock.] (12)	2 [ν , δ] (13, 14)	dp, M_{xy}

Firstly the intense band at 292 cm^{-1} can be attributed to the Ni—Cl bonds, since in NiCl_2 we find two absorptions at 296 and 265 cm^{-1} . Now, for the 21-atomic "molecule," $(\text{CH}_3)_4\text{C}_4\text{Ni}$, 57 n.v. are to be expected. The

TABLE VI
FREQUENCY ASSIGNMENTS FOR $\text{C}_4(\text{CH}_3)_4\text{NiCl}_2^a$

Frequency (cm^{-1})	Type, irreducible representations, and vibration no.
2941 (s)	CH stretch, E (13)
2890 (s)	CH stretch, A_1 (10)
2304 (vw)	2941—617
2151 (vw)	617+1541
1541 (s)	Ring CC stretch, E (5)
1440 (vs)	CH_3 -deformation asym., E (14)
1355 (m)	CH_3 -deformation sym., A_1 (11)
1289 (w)	292+998
1067 (s)	CH_3 -rocking, E (12)
1009 (w)	Ring CC stretch, A_1 (1)
998 (vs)	$\text{C—(CH}_3)$ stretch, E (6)
776 (w)	1067—292
617 (m)	$\text{C—(CH}_3)$ stretch, A_1 (2)
467 (m, br)	Ni—ligand deformation, E (9)
416 (m)	Ni—ligand stretch, A_1 (4)
292 (vs)	Ni—Cl stretch, possibly containing (7)

^a From refs. (52, 36).

frequencies of the four methyl groups, however, will fall together, as if only one group were present. Therefore, we can determine the number of bands according to symmetry C_{4v} (Table IV) and superimpose the spectrum of a C—CH₃ grouping according to C_{3v} (Table V). Thus six n.v. of the C—CH₃ grouping and eight of the Ni—C₄X₄ system should be infrared-active. However, the C—CH₃ stretching (no. 2) vibration A_1 has been counted in both tables. Therefore, in the IR spectrum of NiC₄(CH₃)₄ there will be $4A_1(C_{4v}) + 5E(C_{4v}) + 2A_1(C_{3v}) + 3E(C_{3v}) = 14$ normal frequencies, 12 of which originate from the hydrocarbon ligand.

On the basis of these numbers and some additional facts, a frequency assignment for the complex has been given (52, 36) (Table VI).

2. " π -C₄H₄AgNO₃"

A complex containing the ion π -C₄H₄Ag⁺ was claimed as a product of the reaction between tricyclooctadiene and silver ion. A preliminary frequency assignment was given (53).

In the infrared spectrum of this complex obviously no silver atom-ligand frequency can be assigned. This is in accord with the observation that in silver-olefin complexes such a frequency cannot usually be attributed to a particular band.

The position of the asymmetric C—C stretch of the "double bonds" at 1475 cm⁻¹ is especially interesting, since it lies approximately at the place of the analogous vibration of benzene. In comparison, the same frequency appears at 1541 cm⁻¹ for the tetramethylcyclobutadiene nickel complex, and at 1566 cm⁻¹ for free cyclobutene.

Other intense bands in the IR spectrum did not yield definite clues as to whether the original tricyclic hydrocarbon still is present in the complex or whether cyclobutadiene is the ligand. The number of bands in the infrared spectrum of the complex ion was used to find the most probable structure. Considering Table VII, which lists the numbers of ligand frequencies of the monomeric and dimeric complexes, [C₄H₄Ag]⁺ or [C₈H₈Ag₂]²⁺, the monomeric C_{2h} symmetry seemed to explain the observed bands most plausibly. Moreover since NMR measurements yielded only one proton signal the monomeric structure of Fig. 3 was proposed (54). Very recently, however, NMR results on *trans*- and *cis*-tricyclooctadiene, as well as on the corresponding silver complexes, showed that in the NMR spectra of the dissolved silver complexes two proton signals appear, provided the samples are measured shortly after solution (55). Nevertheless, on standing the two

TABLE VII
NUMBERS OF LIGAND VIBRATIONS OF $[\text{C}_4\text{H}_4\text{Ag}]_n^+ (n = 1 \text{ OR } 2)^a$

	$[\text{C}_4\text{H}_4\text{Ag}]^+$				$[\text{C}_8\text{H}_8\text{Ag}_2]^{2+}$	
	C_{4v}	C_{2v}	C_{2h}	C_s	C_{2v}	C_{2h}
Infrared-active	7	13	9	18	31	21
Raman-active	13	18	9	18	42	21
Inactive (forbidden)	1	—	—	—	—	—

^a Degenerate vibrations are counted only once.

signals disappear, and the previously reported single one, belonging to an anomalously low signal of a cyclooctatetraenesilver complex, is observed. Therefore " $\text{C}_4\text{H}_4\text{Ag}^+$ " should be reformulated as $[\text{C}_8\text{H}_8\text{Ag}_2]^{2+}$. It remains difficult, however, to assign the correct number of infrared frequencies.

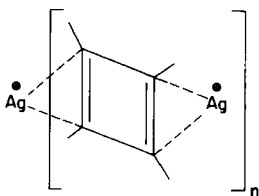


FIG. 3. Proposed $[\text{C}_4\text{H}_4\text{Ag}]^+$ structure.

VII

EXPERIMENTAL RESULTS FOR FIVE-MEMBERED RINGS

A. Cyclopentadienyl Anion, $(\text{C}_5\text{H}_5)^-$

The metal cyclopentadienyls represent the largest group of the non-classical organometallics, i.e. of those compounds which do not have localized σ bonds between metals and organic entities, but σ or π bonds between the metals and systems of delocalized electrons. It is surprising therefore that no complete vibrational spectrum of the parent compound of the entire class, the cyclopentadienyl anion $(\text{C}_5\text{H}_5)^-$, has as yet been

described, although the anion has been known since the early studies of Thiele (56) in 1901. Recent measurements of the Raman and IR spectrum, however, showed that the assumed and most probable pentagonal planar structure with D_{5h} symmetry does indeed exist.

Table VIII shows the spectral expectations for $(C_5H_5)^-$ according to a D_{5h} symmetry. As has already been stated, only four n.v. are infrared-active, while seven n.v. should be found in the Raman spectrum.

TABLE VIII
SPECTRAL EXPECTATIONS FOR THE ANION $(C_5H_5)^-$ WITH D_{5h} SYMMETRY

D_{5h}	C_{5H_5}	C_5	C—H	Activity
A'_1	2	1 [ω]	1 [ν]	p, ia
A''_1	—	—	—	fb, ia
A'_2	1	—	1 [δ]	fb, ia
A''_2	1	—	1 [γ]	fb, M_z
E'_1	3	1 [ω]	2 [ν, δ]	fb, M_{xy}
E''_1	1	—	1 [γ]	dp, ia
E'_2	4	2 [ω, Δ]	2 [ν, δ]	dp, ia
E''_2	2	1 [Γ]	1 [γ]	fb, ia

Because of the large difference in electronegativity, the bonding in C_5H_5Cs should have the most pronounced ionic character of all the metal cyclopentadienyls. Therefore, the "purest" spectrum of the anion should be obtainable with this compound. However, the sensitivity of the alkali metal cyclopentadienyls towards oxidation rises and the solubility in suitable solvents falls with increasing atomic weight of the metal. Because of these properties, more satisfactory results are obtainable with C_5H_5K . These results are listed in Table IX.

Because of the good agreement between the expected and observed spectra there is good reason to consider the D_{5h} symmetry of the anion to be proved.

B. Metal Cyclopentadienyls

If the pure metal cyclopentadienyls are classified according to the number of cyclopentadienyl rings present in the compounds, we must consider four classes, the mono-, di-, tri-, and tetracyclopentadienyls. Additionally, there is one example of a hexa-derivative, $(C_5H_5)_6W$. In all

TABLE IX
VIBRATIONAL SPECTRUM OF C_6H_5K IN SOLUTION

Frequency (cm^{-1})	Irreducible representation (D_{5h})	Type of vibration ^a	Activity
3096	E'_2	(XI)	dp, ia
3043	A'_1	(II)	p, ia
3039	E'_1	(VI)	fb, M_{xy}
1455	E'_1	(V)	fb, M_{xy}
1447	E'_2	(IX)	dp, ia
1020	E'_2	(XII)	dp, ia
1003	E'_1	(VII)	fb, M_{xy}
983	A'_1	(I)	p, ia
710	A''_2	(IV)	fb, M_z
625	E'_1	(VIII)	dp, ia
565	E'_2	(X)	dp, ia

^a The Roman numerals in parentheses () designate the schematic vibration sketches of Fig. 4.

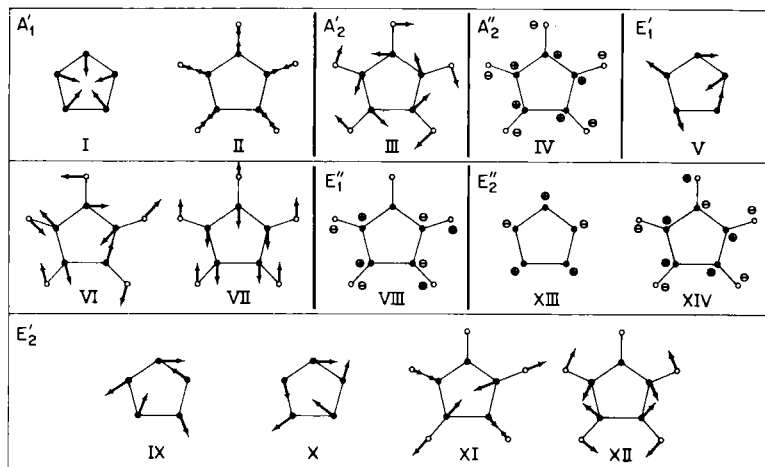


FIG. 4. Schematic sketch of vibrations of cyclopentadienyl anion.

cases, the C_5H_5 ligands can assume the structure shown in Fig. 5a or 5b. Figure 5b shows that the high symmetry of the free anion is lowered to C_{5v} (i.e. the symmetry of a pentagonal pyramid) by covalent bonding to a metal.

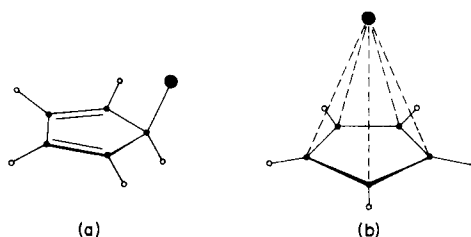


FIG. 5. Structure of cyclopentadienyl ligand.

Table X gives the spectral expectations for this point group, including the metal atom. Figure 5a can be derived easily from free cyclopentadiene by substitution of one of the methylene hydrogen atoms by a metal atom. The original C_{2v} symmetry of cyclopentadiene is thereby lowered to C_s . The spectral expectations for this symmetry group are given in Table XI.

TABLE X
SPECTRAL EXPECTATIONS FOR $(C_5H_5)M$ WITH C_{5v} SYMMETRY

C_{5v}	$(C_5H_5)M$	C_5H_5	C_5	C—H	M—Ligand	Activity
A_1	4	3	1 [ω]	2 [ν , γ]	1 [ω]	p, M_z
A_2	1	1	—	1 [δ]	—	fb, ia
E_1	5	4	1 [ω]	3 [ν , δ , γ]	1 [Γ]	dp, M_{xy}
E_2	6	6	3 [ω , Δ , Γ]	3 [ν , δ , γ]	—	dp, ia

A comparison between the situation with C_{5v} symmetry with that of the D_{5d} symmetry of sandwich complexes of the ferrocene type shows, as expected from the results already discussed in Section IV of this chapter, that in each case the same seven n.v. are to be expected for the C_5H_5 ligands in $Fe(C_5H_5)_2$, regardless of whether the spectrum is interpreted by “local

TABLE XI
SPECTRAL EXPECTATIONS FOR $(C_5H_5)M$ WITH C_s SYMMETRY

C_s	$(C_5H_5)M$	C_5H_5	C_5	C—H	M—Ligand	Activity
A'	15	13	5 [3ω , Δ , Γ]	8 [4ν , 2δ , 2γ]	2 [ω , Δ]	p, M_{xy}
A''	12	11	4 [2ω , Δ , Γ]	7 [2ν , 3δ , 2γ]	1 [Γ]	dp, M_z

symmetry" of the ligands or by the entire symmetry of the complex. Table XII gives the spectral expectations for sandwich molecules of the type discussed.

TABLE XII
SPECTRAL EXPECTATIONS FOR $(C_6H_5)_2M$ WITH D_{5d} OR D_{5h} SYMMETRY

D_{5d}	D_{5h}	$(C_6H_5)_2M$	C_5H_5	C_5	C—H	M—Ligand	Activity
A_{1g}	A'_1	4	3	1 $[\omega]$	2 $[\nu, \gamma]$	Sym. stretch	p, ia
A_{1u}	A'_1	2	1	—	1 $[\delta]$	Torsion	fb, ia
A_{2g}	A'_2	1	1	—	1 $[\delta]$	—	fb, ia
A_{2u}	A'_2	4	3	1 $[\omega]$	2 $[\nu, \gamma]$	Assym. stretch	fb, M_z
E_{1g}	E'_1	5	4	1 $[\omega]$	3 $[\nu, \delta, \gamma]$	Sym. ring tilt	dp, ia
E_{1u}	E'_1	6	4	1 $[\omega]$	3 $[\nu, \delta, \gamma]$	Assym. ring tilt, deformation	fb, M_{xy}
E_{2g}	E'_2	6	6	3 $[\omega, \Delta, \Gamma]$	3 $[\nu, \delta, \gamma]$	—	dp, ia
E_{2u}	E'_2	6	6	3 $[\omega, \Delta, \Gamma]$	3 $[\nu, \delta, \gamma]$	—	fb, ia

Based on these principles it is possible to make a frequency assignment for ferrocene. Both practically and historically this problem has fulfilled a special role in this field. For simplicity, the abbreviation Cp will be used for C_5H_5 , in conformity with international usage. Thus, for example ferrocene will be written as Cp_2Fe .

1. Frequency Assignment for Ferrocene

Lippincott and Nelson proposed the first frequency assignments for ferrocene and ruthenocene in 1958. The results were based on the infrared spectra in dissolved and gaseous states as well as on the Raman spectrum (16, 17). These assignments were subsequently used as a basis for single crystal studies (40) and a comparison of the spectra of a series of cyclopentadienyls of different metals (57). A recent, more exact study of the Raman spectrum of ferrocene, including polarization measurements, enabled Stammreich and co-workers (58) to assign the four most intense lines of the spectrum unequivocally to totally symmetric vibrations. A revision of the assignment of a few bands then became necessary.

Lippincott's assignment made possible a ready interpretation of the nature of the strong bands. The two expected ω_{CC} could very plausibly be

TABLE XIII
 FREQUENCY ASSIGNMENT FOR D_{5d} SYMMETRY^a

"In-phase"				"Out-of-phase"		
Irreducible representation	Freq. no.	Frequency (cm ⁻¹)	Approximate type of vibration ^b	Irreducible representation	Freq. no.	Frequency (cm ⁻¹)
A_{1g}	1	3110	CH stretch	A_{2u}	8	3086
	3	1390	Ring breathing		10	1408
	4	306	M-ring stretch		11	478
A_{2u}	9	1104	CH deform (⊥)	A_{1g}	2	1105
A_{2g}	7	(1249)	CH deform ()	A_{1u}	5	(1253)
			Torsion		6	—
E_{1g}	14	818	CH deform (⊥)	E_{1u}	19	814
	16	390	Ring tilt		21	490
			R—M—R deform		22	(170)
E_{1u}	17	3086	CH stretch	E_{1g}	12	3089
	18	1004	CH deform ()		13	998
	20	1408	CC stretch		15	1412
E_{2g}	23	3045	CH stretch	E_{2u}	29	(3035)
	24	1361	CH deform ()		30	(1351)
	26	1527	CC stretch		32	
	27	1054	CCC deform ()		33	(1054)
E_{2u}	31	(1188)	CH deform (⊥)	E_{2g}	25	1184
	34	(567)	CCC deform (⊥)		28	591

^a From Stammreich (58).^b (||) and (⊥) denote vibrating parallel and perpendicular to the z -axis.

attributed to bands at 1408 and 1104 cm⁻¹ as asymmetric and totally symmetric ring breathing modes. Contrary to the assumption that the band at 1104 cm⁻¹ was due to a CC vibration was the fact that this band shows a

steady decrease in intensity as the bonding between metal and ring ligand becomes more and more ionic. Thus in the "saltlike" alkali metal cyclopentadienyls, it disappears completely (57). However, this behavior can be explained by assuming that the deviation from D_{5h} symmetry of the anion to C_{5v} of the covalently bonded ring becomes smaller and smaller when going, for example, from osmocene, Cp_2Os , to CpK . With D_{5h} symmetry, this n.v. is infrared-inactive and therefore vanishes.

In the Raman spectrum Stammreich (58) found the lines at 1105 and 1390 cm^{-1} to be polarized; they must then correspond to a γ_{CH} and a ring breathing. This result invalidates the earlier assignments. A γ_{CH} appearing at 1390 cm^{-1} seems absolutely out of the question—even 1105 cm^{-1} is unusually high—hence this frequency can be attributed only to the ring breathing. As a so-called pseudo-coincidence (real coincidences are forbidden with D_{5d} or D_{5h} symmetry, due to the rule of mutual exclusion), the infrared frequency at 1408 cm^{-1} has to be assigned to two n.v., since there are Raman lines at 1390 and at 1412 cm^{-1} . Because of the relatively large splitting of these two lines, one can conclude that this is, indeed, not a real coincidence as might be expected according to C_{5v} symmetry, but a pseudo-coincidence according to D_{5h} , which arises from the existence of in- and out-of-phase vibrations of the two ring ligands in the molecule (38).

The difference between real and *pseudo*-coincidence might enable a distinction between those complexes in which there is a coupling between ring vibrations through the central atom, and those for which the local symmetry of a single ligand can describe the spectrum of all ligands. The first approach corresponds to the definitely coordinate-covalently bonded types, while all other kinds of bonding fall into the second group. For the latter, a band of medium intensity can very often be observed, which might correspond in position ($1360\text{--}1390\text{ cm}^{-1}$) and intensity to the 1390 cm^{-1} frequency of ferrocene. Table XIII gives the frequency assignment using Raman results of Stammreich and IR values from two sources (40, 57). The n.v. of the irreducible representation E_{2u} were found from spectra of single crystals, where they are infrared-active due to crystal forces.

2. Skeletal Vibrations of the Complexes

As already discussed equal numbers of ligand bands result from following the method of local symmetry or from considering the entire molecule and its point group. This makes it possible to consider the spectra as superpositions of partial spectra of one ligand in C_{5v} , and the molecular skeleton

as a model with only a few vibrating masses. The ligands are regarded as rigid disks when the skeletal or inner vibrations are to be determined. This procedure is particularly appropriate for the nonlinear di-, the tri-, and tetracyclopentadienyls.

Structures of highest symmetry for complexes with 1, 2, 3, or 4 Cp ligands are the pentagonal pyramid, pentagonal bipyramid or antiprism, equilateral triangle, and tetrahedron. With the equilateral triangle and tetrahedron the ring ligands lie at the corners and apices, respectively. These structures should occur primarily for complexes with predominantly ionic bonding between metal and rings, due to simple electrostatic effects. For covalently bonded complexes deviations from the regular structures can be readily conceived. In the case of localized σ -bonded compounds the high symmetries are completely destroyed.

The number of inner vibrations can be calculated by determining the total number according to the $(3N - 6)$ rule, and subtracting the numbers of the ligand frequencies. For cyclopentadienyls there are $[(3 \times 10) - 6] = 24$ vibrations per ligand. Thus, for Cp_2Fe we should find $[57 - (2 \times 24)] = 9$ skeletal or inner vibrations. Of course, these inner vibrations will correspond to actual bands in the spectra only if the complexes are covalently bonded. A purely electrostatic compound will not have any definite metal-ring bond and consequently no corresponding bond force constants.

a. *Monocyclopentadienyls*. For the two structures of Fig. 5a and b, the symmetry groups C_s and C_{5v} are valid, respectively. The metal-ring vibrations are listed in Table XIV.

TABLE XIV
INNER VIBRATIONS OF MONOCYCLOPENTADIENYL METAL COMPOUNDS

Type of vibration	C_s		C_{5v}	
	Irreducible representation	Activity	Irreducible representation	Activity
Metal-ring stretch	A'	p, M_{xy}	A_1	p, M_z
Metal-ring deformation ()	A'	p, M_{xy}	E	dp, M_{xy}
Metal-ring deformation (\perp)	A''	dp, M_z		

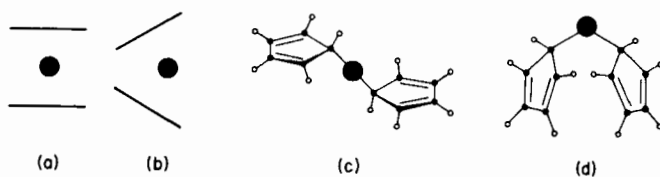


FIG. 6. Possible structures of dicyclopentadienyl molecules.

b. *Dicyclopentadienyls*. The structures of Fig. 6a, b, c, and d will belong to the symmetry groups D_{5d} or D_{5h} , C_i , C_{2v} and C_i or C_1 , respectively. In addition steric variations are possible. These will not be discussed here. All in all, as previously stated nine n.v. can be expected, some of which will be inactive due to symmetry; others may not be observable separately because of degeneracy.

Linearly arranged molecules. For such complexes, structures a and c of Fig. 6 should be considered. Structure a, the real sandwich configuration, can have the ring ligands either fixed in a staggered position, fixed in an eclipsed position, or freely rotating about the ring-metal axis. These three possibilities correspond to D_{5d} , D_{5h} , and D_5 symmetries respectively. It should be stated, however, that free rotation, the third possibility, also leads to the same spectral expectations as the other two. This result confirms the procedure of employing local symmetry considerations. Table XV shows

TABLE XV

INNER VIBRATIONS OF LINEAR DICYCLOPENTADIENYL METAL COMPOUNDS

Type of vibration	D_{5d}		D_{5h}		C_i	
	Irreducible representation	Activity	Irreducible representation	Activity	Irreducible representation	Activity
Symm. metal-ring stretch	A_{1g}	p, ia	A'_1	p, ia	A_g	p, ia
Torsion	A_{1u}	fb, ia	A''_1	fb, ia	A_u	fb, M_{xyz}
Asymm. metal-ring stretch	A_{2u}	fb, M_z	A''_2	fb, M_z	A_u	fb, M_{xy}
Symm. ring tilt	E_{1g}	dp, ia	E'_1	dp, ia	$A_g + A_u$	—
Asymm. ring tilt	E_{1u}	fb, M_{xy}	E'_1	fb, M_{xy}	$A_g + A_u$	—
R—M—R deformation	E_{1u}	fb, M_{xy}	E'_1	fb, M_{xy}	$A_g + A_u$	—

the spectral expectations for D_{5d} and D_{5h} , and for structure d with C_i symmetry. Figure 7 illustrates schematically these nine n.v. The twofold degenerate modes are shown with only one component; these degenerate vibrations will naturally be split in C_i symmetry.

For the two fivefold symmetries, the same three normal vibrations are infrared- and Raman-active, so that a distinction between these symmetries cannot be made spectroscopically. For C_i there will be five infrared- and four Raman-active n.v. These same three n.v. appear for all sandwich complexes, e.g., $Cr(C_6H_6)_2$. However, for XYZ models instead of YXY models

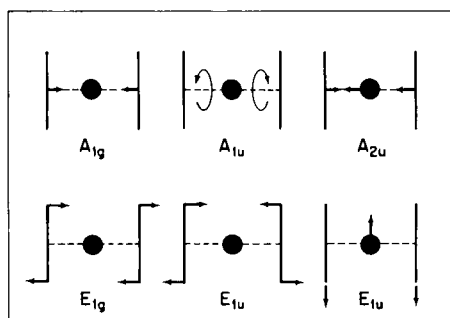


FIG. 7. Normal vibrations for linear dicyclopentadienyl molecule.

(e.g. $C_5H_5CrC_6H_6$ or $C_5H_5VC_7H_7$), all seven normal frequencies should appear in the IR spectrum.

Angular dicyclopentadienyls. For angular metal dicyclopentadienyls, only the structures b and d of Fig. 6 will be discussed. Depending on the position of the rings—eclipsed or staggered—the symmetries will be either C_{2v} or C_s for structure b. If the rings are bent in different ways, C_{2v} or C_1 will apply to structure d. To illustrate the relation of these point groups to D_{5d} , Table XVI lists the symmetry behavior of the nine n.v.

The schemes of the vibrational modes can be derived from those of linear complexes. The main difference is that one of the n.v. originating in the E_{1u} deformation of D_{5d} becomes a “torsional” mode during which the central atom vibrates perpendicularly to the y -axis and to the normal ring-metal-ring deformation. Since the doubly degenerate normal vibrations of D_{5d} split up in the other three groups, seven n.v. will be infrared-active in C_{2v} , while all nine vibrations are infrared-active for C_i and C_1 , and in the Raman spectra.

TABLE XVI
INNER VIBRATIONS OF ANGULAR DICYCLOPENTADIENYL METAL COMPOUNDS

Type of vibration	D_{5d} Irreducible representa- tion	C_{2v}		C_s	
		Irreducible representa- tion	Activity $z \rightarrow y$ $\sigma_h \rightarrow \sigma_v(xz)$	Irreducible representa- tion	Activity
Symm. metal-ring stretch	A_{1g}	A_1	p, M_z	A'	p, M_{xy}
Torsion	A_{1u}	A_2	dp, ia	A''	dp, M_z
Asymm. metal-ring stretch	A_{2u}	B_2	dp, M_y	A''	dp, M_z
		A_2	dp, ia	A''	dp, M_z
Symm. ring tilt	E_{1g}	B_2	dp, M_y	A''	dp, M_z
		A_1	p, M_z	A'	p, M_{xy}
Asymm. ring tilt	E_{1u}	B_1	dp, M_x	A'	p, M_{xy}
		A_1^4	p, M_z	A'	p, M_{xy}
R—M—R deformation	E_{1u}	B_1	dp, M_x	A'	p, M_{xy}

c. *Tricyclopentadienyls*. The discussion of the inner vibrations of this class of substances will be restricted to two structures, Fig. 8a and b, possessing the symmetries D_{3h} and C_{3v} . A molecule with three centrally bonded cyclopentadienyl rings can, of course, also belong to C_{3v} .

The fifteen expected n.v. will distribute among the different irreducible representations as is shown in Table XVII. There are four and eight vibrations infrared-active and six and eight vibrations Raman-active, for D_{3h} and C_{3v} , respectively. Table XVII explains the distribution of the n.v. over the irreducible representations of these two point groups. In addition structures with one "symmetrized" (i.e. pentagonal-symmetric) and two

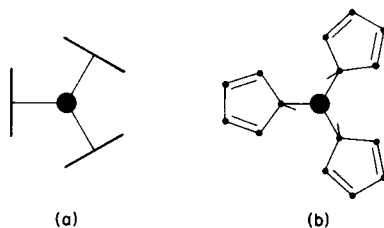


FIG. 8. Possible structure of tricyclopentadienyl molecules.

σ -bonded diene ligands (and vice versa) are possible. Indeed, they can be observed for some complexes. The steric differences make a general discussion of the skeletal vibrations difficult. Because the highest possible symmetry would be C_{2v} , almost all inner vibrations can be expected to be infrared- and Raman-active.

TABLE XVII
INNER VIBRATIONS OF TRICYCLOPENTADIENYL METAL COMPOUNDS

Type of vibration	D_{3h}		C_{3v}	
	Irreducible representation	Activity	Irreducible representation	Activity
Symm. metal-ring stretch	A'_1	p, ia	A_1	p, M_z
Symm. torsion	A''_1	fb, ia	A_2	fb, ia
Ring tilt, in-phase (\parallel)	A'_2	fb, ia	A_2	fb, ia
Symm. deformation	A''_2	fb, M_z	A_1	p, M_z
Ring tilt, in-phase (\perp)	A''_2	fb, M_z	A_1	p, M_z
Asymm. metal-ring stretch	E'	dp, M_{xy}	E	dp, M_{xy}
Asymm. deformation	E'	dp, M_{xy}	E	dp, M_{xy}
Asymm. torsion	E''	dp, ia	E	dp, M_{xy}
Asymm. ring tilt, out-of-phase (\parallel)	E''	dp, ia	E	dp, M_{xy}
Asymm. ring tilt, out-of-phase (\perp)	E''	dp, ia	E	dp, M_{xy}

d. *Tetracyclopentadienyls*. This group of complexes has been studied only very recently. The highest possible symmetry is tetrahedral with four cyclopentadienyl rings at the apices. Again there are several possible arrangements of the four ligands with varying numbers of π - and σ -bonded rings (the latter being diene systems). Of the 117 n.v. expected for $M(C_5H_5)_4$, 96 belong to the four ligands, so that 21 inner vibrations will remain. Of these 21 vibrations nine will belong to the MX_4 system, with the ligands as point masses, and twelve will be torsional and tilting modes of the ligands as rigid disks. They are all listed in Table XVIII.

e. *Expected Band Positions*. From comparison with isosteric XYX , XY_3 , and XY_4 molecules it can be presumed that the asymmetric stretching modes will appear at frequencies lower than 600 cm^{-1} , probably even lower than 500 cm^{-1} . The asymmetric ring-tilt frequency, as has been shown for

Cp_2Fe , Cp_2Ru (17), and $(\text{C}_6\text{H}_6)_2\text{Cr}$ (38), always occurs higher than the asymmetric stretch (59). The infrared-active ring-metal-ring deformation modes can be assigned approximately at half the value of the symmetric stretch, i.e. below 200 cm^{-1} . These modes, therefore, cannot be detected by the usual IR spectrometers. The Raman-active symmetric stretches and ring tilts, as well as the other possible n.v. appear at markedly lower frequencies than the asymmetric ones. Thus, for metal cyclopentadienyls having the most symmetrical arrangement one can normally observe in the infrared spectrum only two n.v. of the molecular skeleton.

TABLE XVIII
INNER VIBRATIONS OF TETRACYCLOPENTADIENYL METAL COMPOUNDS

Type of vibration	Irreducible representation (T_d)	Activity	Vibrator
Totally symm. metal-ring stretch	A_1	p, ia	MX_4
Totally symm. torsion	A_2	fb, ia	Ligands
Metal-ring deformation (twist)	E	p, ia	MX_4
Ring-tilt (2 and 2)	E	p, ia	Ligands
Asymm. metal-ring stretch	F_2	dp, M_{xyz}	MX_4
Metal-ring deformation	F_2	dp, M_{xyz}	MX_4
Asymm. torsion	F_2	dp, M_{xyz}	Ligands
Asymm. torsion	F_2	dp, M_{xyz}	Ligands
Asymm. ring tilt	F_2	dp, M_{xyz}	Ligands

3. Discussion of the Spectra

On the basis of the principles outlined in the preceding sections, the spectra of most of the known cyclopentadienyl complexes will be discussed briefly. In most cases and unless otherwise stated the reported frequencies are from the spectra of samples of the various compounds prepared by Professor E. O. Fischer and co-workers at the Institute of Inorganic Chemistry of the University of Munich, Germany. In order to make this review as complete as possible some as yet unpublished results have been included. Most of the data were obtained with prism instruments.

From chemical and spectroscopic evidence, it is known that bonding in the metal cyclopentadienyls can be of different types. In this section a distinction is made according to the spectroscopic results. Ionic bonding is

assumed for those compounds which show essentially the spectrum of the $(C_5H_5)^-$ anion (cyclopentadienides). Localized σ bonding is assumed for those compounds where the ligands still have, according to their absorptions, diene character, as in cyclopentadiene itself. Complex bonding is assumed for those compounds which show a ligand spectrum corresponding to the local symmetry C_{5v} . However, for "technical" reasons, this last group should be subdivided into one group of complexes having *metal-ring* vibrations in the observable far infrared or Raman spectra and another group of compounds which do not have absorptions attributable to such vibrations in the accessible spectral range down to 250 cm^{-1} in the infrared. Although this distinction might seem rather artificial, it does have a real significance in that the complex bonding is in some cases so weak that no vibration can be observed in the region in which complexes of the ferrocene type normally absorb. In the following sections, therefore, mention is made of ligands bonded by (genuine) π bonds and ligands bonded by *central σ bonds* (from the metals to the center of the symmetrical C_5H_5 rings). Of course, there are also intermediate stages between the four classes, and a strict classification of some compounds is impossible.

General results are tabulated, and therefore no detailed discussion is given in most cases. Exact deductions are somewhat difficult to draw from spectra obtained from polycrystalline samples, as are most of those reported here, due to the influence of factor- and site-groups in the crystals. However, experience shows that those n.v. to be expected for a single molecule usually appear with much greater intensity than those which become active only in the crystalline state. Therefore, in general all the necessary chemically interesting conclusions can be obtained from solid state spectra.

a. *Cyclopentadienyl Ligands Bound Electrostatically.* For this group of compounds no bands due to any metal-ring or metal-carbon interactions should be observable in the vibrational spectra as strong bands; only the four n.v. of the $(C_5H_5)^-$ anion should appear. Typical members of this bond type are the cyclopentadienyls of the heavier alkali and alkaline earth metals. Surprisingly also the transition metal cyclopentadienyl Cp_2Mn shows no absorptions in the far infrared region and also no band at 1100 cm^{-1} typical of π - and centrally σ -bonded complexes. Weak coupling of ring frequencies, despite ionic bonding, can explain the appearance of a band at 1364 cm^{-1} and a C—H deformation at 737 cm^{-1} , which should not be present for predominantly electrostatic compounds. The four n.v. due to the D_{5h} symmetry of each of the compounds of Table XIX are definitely the most intense bands

in the infrared spectra. The Raman data for CpK have previously been given during discussion of the $(C_5H_5)^-$ anion. In addition, especially for the dicyclopentadienyls, there are new bands which are probably due to a weak coupling of the two rings through a "covalent" bonding component, and also due to activation of n.v. in the crystalline state. Thus, bands always appear near 630, 663, and 1235 cm^{-1} which might correspond to deformations of C—C—C and C—H bonds. As can be seen from the solution spectrum of CpK, these moderately intense bands are not observed in the dissolved state.

TABLE XIX

NORMAL VIBRATIONS OF CYCLOPENTADIENYL LIGANDS (D_{5h}) IN IONIC COMPOUNDS^a

Vibration	CpK	CpRb	CpCs	Cp ₂ Ca	Cp ₂ Sr	Cp ₂ Ba	Cp ₂ Mn
ν_{CH}	3048	3030	3021	3049	3077	3065	3049
ω_{CC}	1455	(1501)	1494	1499	1464	1435	(1423)
							1364
δ_{CH}	1009	1011	1008	1006	1006	1009	1000
γ_{CH}	702	696	668	760	745	736	762/737

^a Frequencies in cm^{-1} .

Table XIX shows clearly that with increasing atomic weight the γ_{CH} is shifted to lower frequencies for mono- and dicyclopentadienyls. Since the difference of the electronegativities of metals and cyclopentadienyl ligands also increases in this direction, one can conclude that the more ionic is the character of the bonds or the higher the localization of the original π -electron sextet at the five-membered ring, the lower this frequency will appear.

b. *Centrally σ -Bonded Cyclopentadienyl Ligands.* In general, the spectra of σ -bonded symmetric cyclopentadienyl ligands of this group cannot have the "isolated" symmetry D_{5h} of the cyclopentadienyl anion. They possess a local symmetry C_{5v} . The one-sided bonding to the metal, and, therefore, the absence of the σ_h and the five C_2 's of D_{5h} cause this lowering of symmetry. Due to the lower force constants of the " σ single bonds," in comparison with the π multiple bonds of ferrocene-type complexes, metal-ring vibrations can be observed only with the CsBr prism, and then only for compounds of central metals of low atomic weight. In principle, however, they must be observable. For Li- and NaCp, absorptions which do not belong to

the ring system can be observed at 538 and 315 cm^{-1} . Shigorin *et al.* (60) have assigned Li—C bond frequencies near 1050 cm^{-1} for monomeric, and near 850–930 cm^{-1} for polymeric species. Therefore, the intense 538 cm^{-1} band is assigned to a Li—ligand vibration. Recent work on lithium-organics (61) attributed bands for $C_6H_5-^7\text{Li}$ at 378 and 421 cm^{-1} to complex Li—C movements of polymeric molecules. Therefore, LiCp (and NaCp, which is similar to its homolog) can be classified in this group. By using the harmonic oscillator equation [Eq. 1, Section XI] approximate force constants of the metal—Cp bond of 1.1 and 1.0 $\text{mdyne}/\text{\AA}$ were determined.

Similar situations prevail for Cp_2Be and Cp_2Mg . Although the bonding in Cp_2Mg has generally been considered to be ionic, the long-wavelength bands typical for sandwich complexes of the ferrocene type appear in the IR and Raman spectra (57, 62). Only reluctance to assume participation of *d*-electron orbitals of Mg in the bonding prevents classification of Cp_2Mg as a genuine π complex, from the spectroscopic point of view. Thus, the idea of a covalent central σ -type bond seems to be a good compromise.

An ionic bond was once also proposed for CpTl (39), but chemical evidence, such as preparation in aqueous medium and readiness to sublime, indicates a more covalent bond character. Again in this case, assumption of a central σ bond solves the problem, since no far-infrared absorption is found and the typical γ_{CH} appears at 730 cm^{-1} . This “covalent” compound would have only a relatively weak σ bond from metal to ligand.

For obvious reasons, all complexes showing no metal—ligand bands must also be included in this group of compounds. This is especially true if a dipole moment (as in Cp_2Sn) suggests an angular structure implying the absence of purely electrostatic bonds (63). This view can be modified only if the 1100 cm^{-1} band is not observed. This is the case for ionic cyclopentadienyls, as previously stated. Table XX lists all cyclopentadienyls which have the Cp ligands entirely or partially bonded by central σ bonds. Those main group elements, lanthanides, and actinides which possess filled *d* and *f* shells, all show this “central σ bonding.” Within any particular group of the periodic system, the γ_{CH} near 750 cm^{-1} is lowered with decreasing atomic weight. This is also observed if several rings are bound to a metal or with increasing oxidation number if several oxidation states of one metal are known to undergo complex formation. One must conclude that a decrease in bond strength parallels this lowering of frequency.

By comparison with the electrostatic cyclopentadienyls it appears that with both ionic and central σ bonds, the same change in the 700–800 cm^{-1}

band can be observed. Therefore, the so-called "central σ bond" complexes should have an essentially ionic component in their metal-to-ring bonds.

Again, in addition to the expected seven IR-active n.v. of point group C_{5v} , there are other absorptions corresponding to combination bands of n.v. activated by crystal field forces.

TABLE XX

NORMAL VIBRATIONS OF "CENTRALLY σ -BONDED" CYCLOPENTADIENYL LIGANDS (C_{5v})^{a, b}

Compound	1	2	3	4	5	6	7	8
LiCp	3048	2906	1426	1120	1003	?	746	538
NaCp	3048	2907	1422	(1144)	998	?	712	315
BeCp ₂	3067	2941	1433	1121	1008	744	738	414
MgCp ₂	3067	2913	1428	1108	1004	779	758	439
LaCp ₃	3081	2932	1436	1116	1009	787	766	—
GaCp ₃	3058	2933	1447	1098	?	?	744	—
TlCp	3049	2916	1423	1121	1003	753	734	—
UCp ₃	3086	2967	1443	?	1012	820	792	—
[UCp ₃] ⁺	3067	2924	1437	1121	1010	816	785	—
UCp ₄	3077	2924	1447	?	1010	789	782	—
ThCp ₄	3068	2916	1441	?	1008	788	778	—
SnCp ₂	3065	2924	1428	1114	1004	788	758	—
PbCp ₂	3021	2914	1416	1112	1007	752	740	—
ZrCp ₄	3086	2933	1422	1098	1007	?	749	—
HfCp ₄	3058	2924	1435	1109	1010	?	732	—
BiCp ₃	3058	2924	1412	1109	993	773	738	—
CpVCl ₂	3077	2916	1433	1126	1008	869	824	—
TaCp ₄	3077	2924	1423	1107	1006	832	765	—
MoCp ₄	3067	2907	1423	1102	1012	826	750	—

^a The frequencies of columns 1 to 7 correspond to the seven n.v. of $M(C_5H_5)$ infrared-active in C_{5v} (cf. Table X). Column 8 lists the observed metal-ring stretching frequencies. The assignments of 1 and 2 are tentative, 1 being possibly the *E*-representation vibration, the A_1 vibration being unobserved.

^b Frequencies in cm^{-1} .

c. *π -Bonded Pentagonal Symmetric Cyclopentadienyl Ligands.* For compounds with ligands of this type—the genuine " π complexes"—spectra having relatively few bands are to be expected. As already mentioned, in the normally observable spectral range seven infrared-active n.v. of the ligands and two or three n.v. of the molecular skeleton appear. The latter should not

occur at frequencies higher than 600 or 500 cm^{-1} . Almost all transition metals form compounds in this group, especially if carbonyl derivatives are included. The carbonyl derivatives will be discussed in a later section.

In group II of the Periodic System only Zn and Cd seem to form covalently bonded derivatives. Moreover, with elements of group IIIa, no complex with coordinative covalent bonds is known at all. Only metals of the IVth, Vth, VIth, VIIth, and VIIIth subgroups undergo π -complex formation with the C_5H_5 group. This is understandable, since the availability of d electrons permits a mechanism of dative bonding from ligand to metal as well as back-bonding to empty ligand orbitals, a situation sometimes summarized by the term "coordinate-covalent" bonding.

The group VIa metals molybdenum and tungsten "stabilize" their dicyclopentadienyls by addition of two hydrogen atoms to give Cp_2MoH_2 and Cp_2WH_2 . The group VIIa metals Mn, Tc, and Re show different structures for each of their cyclopentadienyl derivatives. For Cp_2Mn , as already stated, we must assume essentially electrostatic bonds between metal and rings, while technetium and rhenium form coordinate-covalent complexes of a different formula type. The inert gas configuration is achieved by dimerization with $[TcCp_2]_2$ (64) and by addition of a hydrogen atom with Cp_2ReH (64a).

Finally, it should be noted that the most stable dicyclopentadienyls, Cp_2Fe , Cp_2Ru , Cp_2Os , and $[Cp_2Co]^+$ are formed by metals of group VIII.

In order to review the largest possible number of ligand and metal-to-ring frequencies some metals not known to form dicyclopentadienyls are represented by derivatives containing only one C_5H_5 ring. Aside from the observation of only seven ligand bands, according to the local (metal-ring) symmetry C_{5v} band shifts of considerable interest can be observed in the spectra. Of course variation of the central metal influences the position of the skeletal frequencies. This will be discussed in a later section. A general trend of shifts of ligand vibrations is obvious for only two of the seven bands; for two of the others, only variations in intensity are evident.

The $A_1(C_{5v})$ or $A_{2u}(D_{5d})$ C—H-stretching vibration usually appears with such low intensity that it is often not apparent. As pointed out, this can be explained by assuming deviations for the angles of the hydrogen atoms out of the Cp plane (39). The $A_1(C_{5v})$ or $A_{2u}(D_{5d})$ C—H deformation (\perp) near 1100 cm^{-1} gives some hint of the degree of ionic bonding between metals and rings in dicyclopentadienyls. For coordinate covalent complexes such as Cp_2Os , Cp_2Ru , or Cp_2Fe , this band always appears strong and quite

constant at 1100 cm^{-1} . As already stated, for ionic compounds containing the $(\text{C}_5\text{H}_5)^-$ anion, this 1100 cm^{-1} absorption disappears, being symmetry-forbidden in D_{5h} . The transition from covalent to ionic derivatives cannot be abrupt. We observe therefore a steady decrease in intensity for the series of cyclopentadienyls. This behavior is paralleled by frequency shifts of two vibrations, the $E(\text{C}_{5v})$ or $E_{1u}(\text{D}_{5d})$ C—C-stretching (asymm. ring breathing) near 1410 cm^{-1} and $E(\text{C}_{5v})$ or $E_{1u}(\text{D}_{5d})$ γ_{CH} near 800 cm^{-1} . With increasing degree of ionic bonding the first one shifts to 1446 cm^{-1} while the second one decreases to about 700 cm^{-1} . Because this shift should also occur in those compounds which do not exhibit metal–ring stretchings in the observable region, its position can be a valuable indication of the type of bonding in dicyclopentadienyls. Table XXI lists the seven assigned infrared-active ligand n.v. of coordinative-covalent complexes as well as the corresponding infrared-active ring tilting and metal–ring stretching vibrations (columns 8 and 9). Again the data, obtained with polycrystalline samples, are from the spectra collection of the Munich group, except for $[\text{Cp}_2\text{Tc}]_2$ (64) and Cp_2TaH_3 (65).

TABLE XXI

IR-ACTIVE NORMAL VIBRATIONS OF π -BONDED CYCLOPENTADIENYL LIGANDS (C_{60})^a

Compound	1	2	3	4	5	6	7	8	9
Cp_2Zn	3047	2906	1410	1106	988	873	760	(613)	345
CpZnC_2H_5	3060	2941	1414	1093	989	782	747	607	?
CpCdC_2H_5	3040	2907	1405	1106	991	833	763	n.m. ^b	n.m.
Cp_3Ti	3048	?	1443	1118	1015	819	746	609	413
						793	716	570	372
Cp_2TiCl_2	3077	?	1441	1130	1015	871	823	595	415
CpTiCl_3	3058	?	1435	1124	1017	816	797	486	414
Cp_2ZrCl_2	3115	?	1441	1133	1014	851	810	n.m.	n.m.
CpZrCl_3	3021	2907	1441	1130	1018	—	832	n.m.	n.m.
Cp_2HfCl_2	3096	?	1445	1125	1014	855	816	?	330
Cp_2V	3086	2933	1425	1106	1006	783	774	422	379
Cp_2VCl	3070	2916	1426	1121	1004	845	810	416	354
CpVCl_3	3086	?	1423	1121	1016	838	826	375	320
CpVC_7H_7	3039	2941	1421	1108	1012	816	803	?	432
					1003				
Cp_3Nb	3077	2916	1433	1120	1007	798	749	n.m.	n.m.
Cp_4Nb	3068	2916	1433	1120	1008	818	747	(459)	(359)

continued.

TABLE XXI (Continued)

Compound	1	2	3	4	5	6	7	8	9
Cp_3TaH_3	3090	?	1425	1117	1020 1005	870 858 848	825 795	n.m.	n.m.
Cp_2Cr	3076	?	1404	1089	987	829	766	429	408
$[Cp_2Cr]^+$	3012	?	1421	1112	1007	835	?	479	381
$[CpCrO]_4$	3049	2916	1433	1114	1006	840	795	(365)	365
$CpCrC_6H_6$	3058	2933	1410	1099	998	780	765	(450)	450
Cp_2MoH_2	3058	2907	1408	1099	1004 985	818 809	763	414	330
Cp_2WH_2	3053	2899	1410	1094	1001 984	820	775	398	312
$CpMnC_6H_6$	3049	2916	1409	1106	1002	808	762	535	483
$[Cp_2Tc]_2$	3100	?	1410	1100	1003 996	803	775	n.m.	n.m.
Cp_2ReH	3034	2915	1408	1096	995 987	816	795	412	351
Cp_2Fe	3086	2909	1408	1104	1001	854	814	490	478
$[Cp_2Fe]^+$	3106	2933	1412	1107	1003	852	817	510	423
Cp_2Ru	3097	?	1410	1101	1002	866	821	446	379
Cp_2Os	3061	2907	1400	1098	998	831	823	428	353
Cp_2Co	3041	?	1412	1101	995	828	778	464	355
$[Cp_2Co]^+$	3106	2916	1414	1103	1008	867	820	500	461
$[CpCoC_6H_6]^+$	3096	?	1419	1111	1012	—	—	477	434
$[Cp_2Rh]^+$	3058	2900	1410	1107	1009	874	847	n.m.	n.m.
$[CpRhC_6H_6]^+$	3096	2967	1419	1111	1031	837	759	n.m.	n.m.
$CpRhC_5H_6$	3086	2958	1409	1102	1006	789	764	n.m.	n.m.
$[IrCp_2]^+$	3077	?	1409	1106	1009	862	818	n.m.	n.m.
$CpIrC_5H_6$	3030	2958	1404	1097	995	810	769	n.m.	n.m.
Cp_2Ni	3052	2891	1421	1109	1002	839	772	?	355
$CpNiC_3H_5$	3044	2990	1404	1108	1009	838	783	451	406
$CpPdC_3H_5$	3066	2932	1400	1102	1011	770	741	582	376

^a Frequencies in cm^{-1} .^b n.m. = not measured.

d. *Cyclopentadienyl Metal Carbonyls and Nitrosyls*. Since this chapter is concerned mainly with the vibrations of Cp ligands, the CO frequencies will be discussed only briefly. Most of the vibrational spectral studies on the structure of cyclopentadienyl metal carbonyls are concerned with investigating the stretching vibrations of the carbon monoxide groups (66–68). In general, these CO stretching vibrations are lowered or raised when the negative or positive charge of the complex is increased. This can be explained by assuming variable occupation of antibonding CO orbitals.

The C_5H_5 ligands of cyclopentadienyl metal carbonyls are, with but few exceptions [e.g. $C_5H_5Fe(CO)_2C_5H_5$, ref. (69)], π -bonded pentagonal symmetric rings. The infrared spectra of a number of carbonyls have been reported in literature. Table XXII lists typical bands of $M-Cp$ systems, mostly obtained using polycrystalline samples. The bands have already been discussed for Cp compounds of transition metals. In columns 1 to 7 the frequencies of the seven C_{5v} n.v. are listed. In column 8 the metal-ring stretching frequencies are given and in 9 and 10 the A_1 and E $C-O$ stretching vibrations of each C_{nv} structure of the $M(CO)_n$ groups. Due to asymmetry of the ring ligands or solid phase influence the degeneracy of the latter band is sometimes removed.

TABLE XXII

IR-ACTIVE C_{5v} NORMAL VIBRATIONS OF THE π -BONDED CYCLOPENTADIENYL LIGANDS IN CYCLOPENTADIENYLMETAL CARBONYLS^a

Compound	1	2	3	4	5	6	7	8	9	10
$Cp_2Ti(CO)_2$	3030	2907	1423	1107	1013 999	810	794	458	1969	1890
$CpV(CO)_4$	3096	?	1427	1122	1012	839	?	353	2016	1916
$[CpV(CO)_3]Cs_2$	3058	?	1427	1109	1018 1003	837	778	n.m.	1849	1748 1733
$CH_3COC_5H_4V(CO)_4$	3165	3145	1427	1120	?	846	?	374	2045	1949
$[CpCr(CO)_3]_2$	3077	?	1425	1114	1017 1011	845	840	371	1946	1901
$CpCr(CO)_3H$	3096	?	1425	1114	1010	834	759	n.m.	2020	1938
$CpCr(CO)_3D$	3096	2907	1423	?	1010	836	706	n.m.	2020	1934
$CpCr(CO)_3CH_3$	3096	2967	1429	1116	1013	867	846	n.m.	2000	1908
$[CpCr(CO)_3]Na$	3068	2899	1425	1114	1000	840	696	n.m.	1880	1695
					813					
$[CpCr(CO)_4]BF_4$	3106	?	1433	1121	1017	878	820	431	2105	2028
$[CpMo(CO)_3]_2$	3115	2950	1439	1110	1011	810	749	330	1942	1862
$CpMo(CO)_3H$	3096	?	1418	1107	1006	842	812	n.m.	2028	1934
$CpMo(CO)_3D$	3086	?	1416	1107	1005	841	814	n.m.	2024	1942
$CpMo(CO)_3Cl$	3096	?	1429	?	1004	838	822	n.m.	2062	1992 1965
$[CpMo(CO)_4]PF_6$	3106	?	1427	1109	1012	880	?	n.m.	2128	2041 1980
$[CpW(CO)_3]_2$	3115	?	1418	1106	1013	841	831	347	1965	1866
$CpW(CO)_3H$	3096	2915	1422	?	1006	840	826	347	2024	1927
$CpW(CO)_3D$	3106	2916	1418	1105	1008	839	826	n.m.	2016	1916

continued.

TABLE XXII (Continued)

Compound	1	2	3	4	5	6	7	8	9	10
$CpW(CO)_3CH_3$	3096	2950	1421	1106	1008	855	833	352	2008	1908
$[CpW(CO)_4]PF_6$	3115	?	1425	1109	1011	880	?	n.m.	2128	2028
$CpW(CO)_3Cl$	3096	?	1428	1107	1005	842	833	352	2045	1961
										1927
$CpW(CO)_3Br$	3086	?	1425	1104	1003	840	833	351	2028	1949
										1905
$CpW(CO)_3I$	3096	?	1420	1106	1008	845	?	348	2041	1953
										1927
$CpMn(CO)_3$	3096	2916	1425	1112	1005	850	835	370	2020	1930
										1923
$CpTc(CO)_3$	3125	?	1418	1103	1009	824	817	437	2040	1949
					1001					
$CpRe(CO)_3$	3135	?	1418	1104	1000	841	824	347	2037	1949
									2024	
$[CpFe(CO)_2]_2$	3096	2924	1416	1116	1014	840	813	384	1942	1770
					997					
$[CpRu(CO)_2]_2$	3115	2933	1409	1107	1011	835	813	358	1946	1746
					993					
$[CpOs(CO)_2]_2$	3086	2933	1407	1103	1007	836	820	316	1953	1908
					998					
$CpCo(CO)_2$	3115	2941	1401	1111	1018	812	756	378	2037	1965
					984					
$CpRh(CO)_2$	3096	2924	1403	1105	1014	829	792	329	2051	1987
					983					
$CpIr(CO)_2$	3125	?	1401	1103	1011	863	812	n.m.	2037	1957
					988					
$[CpNiCO]_2$	3135	2950	1409	1104	1010	803	774	(417)	1873	1828
					989					
$Cp_3Ni_3(CO)_2$	3086	2924	1416	1106	1001	816	794	365	—	1741
$[CpPtCO]_2$	3096	3012	1395	—	1008	829	786	469	2005	1968
$CpPt(CO)I$	3106	3021	1447	1104	1011	829	798	n.m.	2049	—
			1383							

^a Frequencies in cm^{-1} .

In the compounds of the group VIII metals, the 1000 cm^{-1} band is frequently split into two bands appearing slightly below and above 1000 cm^{-1} . The fact that the position of the seven ring vibrations is rather constant is indeed remarkable. This is true even if different substituents are linked to the central atom. For example, in the case of $CpW(CO)_3R$, where R is $-CpW(CO)_3$, $-D$, $-H$, $-CH_3$, $-I$, $-Br$, or $-Cl$ (i.e. with R differing greatly

in electronegativity), good constancy of the ring vibrations is observed. In contrast the A_1 C—O stretching vibration of the $M(CO)_n$ groups varies over the range 1965 to 2045 cm^{-1} . This leads to the conclusion that additional electronic charge is distributed mostly on the CO groups and only to a minor extent on the cyclopentadienyl ligands.

Essentially the same band positions are observed for the ligand rings in the small number of known cyclopentadienyl metal nitrosyls (70, 71).

e. *Cyclopentadienyl Metal Hydrides*. In comparison with the large number of other cyclopentadienyl compounds, only a few cyclopentadienyl complexes having one or more hydrogen atoms linked directly to the metal atom are known. While the cyclopentadienyl hydrides [except Cp_2TaH_3 (65)] are bases, the cyclopentadienyl carbonyl hydrides are acids. The ring ligands in all hydrides are symmetrical and π bonded. Quite recently by protonation of various complexes new "hydrides" have been obtained, e.g. $[\text{Cp}_2\text{FeH}]^+$ (72). Their existence has been proved by NMR spectroscopy and no vibrational spectra have been reported. The metal-hydrogen stretching vibrations of well-established hydrides are listed in Table XXIII together with approximate force constants, determined by Eq. 1 (Section XI). The similarity of the estimated M—H and M—D force constants for the cyclopentadienyl metal carbonyl hydrides confirms the assignments.

On the basis of the measured dipole moment of Cp_2MoH_2 and Cp_2WH_2 , an angular ring-metal-ring arrangement has been postulated. This structure has been confirmed by a study of the far-infrared spectra. Since the hydrochlorides $[\text{Cp}_2(\text{Mo}, \text{W})\text{H}_3]\text{Cl}$ show only two intense bands in the same region for the polycrystalline samples, a parallel position for the two Cp ligands has been assumed (63). However, the proton magnetic resonance spectrum—a typical AB_2 pattern for the three H atoms for the dissolved complexes—suggests the tilted ring structure (10, 65). An X-ray analysis should settle this question. However, the objection to the spectroscopic evidence, namely, that due to studies in the solid state too few bands are to be observed, cannot be valid, for the crystal forces would make even more bands infrared-active than are to be expected for a single molecule in solution.

Finally, a Ti—H band has been reported at 1942 cm^{-1} in the complex Cp_2TiBH_4 (73).

f. *Ring-substituted Cyclopentadienyls*. It was noted early in this field that in the infrared spectra of ferrocene the two intense bands near 1100 and 1000 cm^{-1} correspond to the presence of unsubstituted rings in the complex

(74). Due to its importance for those working on preparative organic ferrocene chemistry the presence or absence of these bands is usually called the "9,10 μ -rule." The rule can be regarded as the first confirmation of the fact, proved by Stammreich's frequency assignment, that these two frequencies involve deformation vibrations of the five ring protons and not, as previously assumed, one perpendicular CH deformation and one ring breathing mode. Hence, in those cases where no vibrations of the substituents mask this particular spectral range, the "9,10 μ rule" permits a distinction between, for example, homoannular 1,2- or heteroannular 1,1'-disubstitution products of ferrocene. A difference even exists between 1,2- and 1,3-derivatives, so that one can obtain valuable help in the determination of the stereochemistry of certain reactions (75).

TABLE XXIII
METAL-HYDROGEN STRETCHING FREQUENCIES OF CYCLOPENTADIENYL
METAL HYDRIDES

Compound	M—H Frequency ^a	f (mdyne/Å)
Cp ₂ ReH	2032/2000	2.34
[Cp ₂ ReH ₂]PF ₆	2055 (72a)	2.5
Cp ₂ ReD	1458/1432	2.38
Cp ₂ MoH ₂	1847	1.99
[Cp ₂ MoH ₃]Cl	1812 (?)	1.96
[Cp ₂ MoH ₃]PF ₆	1915 (72a)	2.19
Cp ₂ WH ₂	1912	2.15
[Cp ₂ WH ₃]Cl	1969/1942	2.24
[Cp ₂ WH ₃]PF ₆	1943 (72a)	2.24
Cp ₂ TaH ₃	1735 (65)	1.77
Cp ₂ TiBH ₄	1942 (73)	2.27
CpFe(CO) ₂ H	1835 (72a)	2.03
CpFe(CO) ₂ D	1330 (72a)	2.16
CpRu(CO) ₂ H	1853 (72a)	2.05
CpRu(CO) ₂ D	1325 (72a)	2.12
CpCr(CO) ₃ H	1828	1.93
CpCr(CO) ₃ D	1299	1.92
CpMo(CO) ₃ H	1808 [1790 (72a)]	1.91
CpMo(CO) ₃ D	1285 [1285 (72a)]	1.91
CpW(CO) ₃ H	1828 [1845 (72a)]	1.96
CpW(CO) ₃ D	1306 [1322 (72a)]	1.99

^a Frequencies in cm⁻¹.

Since this topic is somewhat removed from the subject matter of this chapter, we shall restrict ourselves to giving some important references for further study. Alkyl- and arylferrocenes have been investigated by infrared spectroscopy (75–81), as well as acetyl derivatives (75, 79) or more generally ferrocene-ketones (76, 82, 83). While unsubstituted $(C_5H_5)_2Fe$ can be protonated at the metal (72), some ferrocene-ketones show protonation at the $C=O$ groups (84). Bridged ferrocenes also have been extensively studied (82, 85–87). The relation between ν_{CH} and the degree of substitution has been pointed out for polysubstituted ferrocenes (88).

It was later shown that the “9,10 μ rule” is also valid for the homologs of ferrocene, ruthenocene and osmocene (89, 90) and, in addition, after successful substitution reactions of various other cyclopentadienyls [e.g., $C_5H_5Mn(CO)_3$ (91–94), $C_5H_5V(CO)_4$ (95–97), or $C_5H_5Cr(CO)_2NO$ (98)] had been carried out, for covalent cyclopentadienyls in general. Some cases of apparent failure of the rule have been reported (83, 88). However, this results mainly because of substituent absorption in the 9–10 μ region (99). In addition it should be remembered that the 1100 cm^{-1} band also disappears in ionic cyclopentadienyls.

g. Influence of Number of Ligands, Type of Anions, and Oxidation State of the Metal. Titanium and vanadium derivatives of many different types are known and have been investigated spectroscopically. Table XXIV compares characteristic bands for two series of cyclopentadienyl metal complexes with different anions, with variation of the charged species, and with changing oxidation states. It can be seen that the n.v. in the cyclopentadienyl ring planes are affected only to a minor extent, compared with the γ_{CH} near 800 cm^{-1} . This frequency exhibits a definite shift, paralleling the increase in positive charge at the central atom. Since the in-plane deformation near 1015 cm^{-1} remains constant, one can conclude that the “framework of $C-C$ σ -bonds” within the cyclopentadienyl ligands is not involved in bonding. Formation of bonds from ring ligands to metals would be accomplished by the π electrons, according to molecular orbital theory. Because of small variations in ω_{CC} (no. 3) the metal–ring stretching frequency can be assumed to show a similarly constant position.

If one considers the relationship between γ_{CH} and ionic character, as found for the alkali and alkaline earth metal cyclopentadienyls, the complexes exhibit covalent bonding with those derivatives with higher positive charge on the metal. This is in contrast to the certainly plausible assumption that the unusual stability of ferrocene-type complexes is determined to

major degree by back-donation from the metal into empty π orbitals of the ring ligands. The number of back-bonding electrons is, however, reduced in the higher oxidation states.

TABLE XXIV
INFRARED-ACTIVE NORMAL VIBRATIONS OF TITANIUM AND VANADIUM COMPOUNDS
BETWEEN 1500 AND 250 cm^{-1}

Compound	Frequency number ^a				
	3	4	5	7	9
Cp_3Ti	1443	1128 1118	1015	793	413
Cp_2TiCl	1445	1140	1015	798	350
Cp_2TiBH_4	1440	1123	1015	800	345
CpTiCl_3	1435	1124	1017	816 (797)	414
Cp_2TiI_2	1439	1130	1014	819	n.m. ^b
Cp_2TiBr_2	1441	1130	1015	822	417
Cp_2TiCl_2	1441	1130	1015	823	415
Cp_2TiF_2	1443	1130	1014	823	416
$\text{Cp}_2\text{Ti}(\text{SCN})_2$	1439	1127	1015	831	410
Cp_2V	1425	1106	1004	783 774	379
Cp_2VCl	1426	1121	1004	810	n.m. ^b
Cp_2VCl_2	1433	1126	1008	824	n.m. ^b
CpVCl_3	1423	1121	1016	838 826	375

^a Corresponding to frequency numbers of Table XXI.

^b n.m. = not measured.

Important for spectroscopic analysis of cyclopentadienyl derivatives is the fact that the frequencies of the characteristic bands are virtually constant, when for one particular metal electronegative ligands or the oxidation states are altered.

h. *Diene-type Cyclopentadienyl Ligands.* The Cp ligands discussed in this section correspond spectroscopically to a cyclopentadiene with one of the methylenic protons substituted by a metal. Accordingly, spectra will be observed having a greater number of bands compared with those of symmetrically bound Cp ligands. In the far-infrared region metal-carbon

stretching vibrations should appear, and in the range of the NaCl prism some typical frequencies of C_5H_6 , with only slight shifts. Of these the absorptions of the "free" $C=C$ bonds should be especially observable, although they might have lower intensity in the metal derivatives because the enhancement of intensity by conjugation should be lessened by electron removal towards the metal.

The first infrared spectra of "diene-Cp ligands" were reported in 1956 (100), for Cp_2Hg , $CpCuP(Et)_3$, and $CpSi(CH_3)_3$. In addition to these compounds, as well as in $Cp_2Si(CH_3)_2$, $CpHgI$, Cp_3Al , Cp_2Sn , $CpSn(CH_3)_3$, $CpSn(C_6H_5)_3$, and probably Cp_6W , this type of Cp ligand occurs in complexes of Zr, Hf, Nb, Ta, and Mo also having centrally σ -bonded or

TABLE XXV

INFRARED-ACTIVE NORMAL VIBRATIONS OF σ -BONDED DIENE-TYPE CYCLOPENTADIENYL LIGANDS^a

Compound	1	2	3	4	5	6	7	8	9	f (mdyne/Å)
C_5H_6	1590	1364	1083	990	890	806	756	668	—	—
$CpCuP(C_2H_5)_3$	1530	1380	1050	1000	860	—	753	692	n.m.	—
Cp_2Hg	1529	1372	?	986	920	—	752	610	331	3.2
$CpHgI$?	1372	?	963	917	827	765	610	366	3.9
Cp_3Al	?	1385	?	965	889	824	759	610	475	2.5
Cp_3In	1608	1350	1079	988	895	839	761	612	307	2.3
				971		831	746			
							733			
$(CH_3)_3SiCp$	1518	1383	1062	978	907	818	723	617	413	2.1
$(CH_3)_2SiCp_2$	1595	1381	1060	978	906	818	744	—	451	2.4
							730			
Cp_4Sn	1529	1381	1083	985	891	820	750	634	336	2.9
Cp_4Zn	1582	1389	1030	982	917	829	749	—	(350)	2.6
							730			
							712			
Cp_4Hf	1592	1389	1023	992	—	835	732	614	(296)	2.4
						826	715			
Cp_4Nb	1580	1362	1075	967	980	818	747	619	259	2.9
							710			
Cp_4Ta	1563	1362	1076	975	876	819	725	620	—	—
							708			
Cp_4Mo	1567	1359	1054	986	894	809	750	612	—	—
Cp_6W	1570	1364	—	989	896	835	736	617	—	—

^a Frequencies in cm^{-1} .

π -bonded ring ligands. This can be confirmed by the ability to effect partial hydrogenation and by the results of NMR studies. Table XXV lists the n.v. or typical bands which on the basis of our present knowledge prove the existence of diene-Cp ligands. The intense bands can be derived from the corresponding C_5H_6 frequencies.

In the spectra of the silicon derivatives the $—Si(CH_3)_3$ and $—Si(CH_3)_2$ groups can be identified by bands at 1248 and 749 cm^{-1} and 1248 , 835 , and 751 cm^{-1} , respectively. They correspond to $(CH_3)—Si$ deformation and $Si—C$ stretching vibrations.

In column 9 of Table XXV tentatively assigned metal-carbon stretching frequencies are listed. The tenth column gives the approximate symmetry force constants. These values appear within the range of those of normal organometallic compounds, for example, $(CH_3)_2Hg$ has $f = 2.45\text{ mdyne/\AA}$.

i. *Identification of Cyclopentadienyl Metal Compounds.* From the above discussion it can be seen that four types of bonding between metals and the rings in cyclopentadienyl compounds can be recognized. Considering the local symmetry of the ligands, there are “classical” organometallics (i.e. diene derivatives), as well as symmetrically bound five-membered rings. With the second alternative, bonding can be either predominantly electrostatic, or have mainly σ or have mainly π character. A distinction between these four types is possible with some certainty by infrared spectroscopy. In the spectra of definite “diene-type” derivatives of the cyclopentadienyl group, bands always appear in the eight frequency ranges given in Table XXVI. Thus if in all these regions infrared bands appear simultaneously, one can assume the existence of “ C_5H_5 -diene” ligands (Fig. 5a). Ionic cyclopentadienyl compounds exhibit IR spectra having essentially four intense bands of the $(C_5H_5)^-$ anion. Covalently bound but symmetrically disposed Cp ligands can be clearly identified by the simultaneous appearance of five of the seven n.v. expected from a local C_{5v} symmetry of the metal-ring group. Table XXVII lists the five spectral ranges. Of these five bands those numbered 3 and 5 can provide further indications of bond character, as already mentioned. In general, for sandwich complexes with parallel rings, the γ_{CH} (frequency no. 5) is shifted to higher frequencies with increasing covalency of the metal-to-ring bonding. For example, it is observed at 832 cm^{-1} for Cp_2Os but at 738 cm^{-1} or 712 cm^{-1} for Cp_2Be or $CpNa$, respectively.

The decrease in intensity of the 1100 cm^{-1} band with decreasing covalent bonding can be very informative. This band appears intense in the spectra

TABLE XXVI
TYPICAL BANDS FOR "DIENE- C_5H_5 " LIGANDS

Frequency no.	Frequency range (cm^{-1})	Number of bands	Intensity ^a
1	1529-1610	1	w- <u>m</u>
2	1359-1389	1	<u>m</u> -s
3	1029-1079	1-2	m- <u>s</u>
4	967-1002	1-2	m- <u>s</u>
5	876- 917	1-2	m- <u>s</u>
6	809- 841	1-3	<u>s</u>
7	690- 750	1-4	s- <u>vs</u>
8	610- 620	1	<u>m</u>

^a The most frequent intensities are underlined.

of Cp_2Os , Cp_2Ru , or Cp_2Fe , and is almost imperceptibly weak in the spectra of uranium derivatives or similar compounds. Application of the above-mentioned empirical "guides" has enabled the establishment of a number of structures previously not clearly understood. Thus although for Cp_2Hg only one proton resonance signal can be observed, the structure can be established definitely as that of a "classical" organomercurial, as previously assumed (100). On the other hand for Cp_2Be , Cp_3Bi , or Cp_3Sb the sole existence of symmetrically bound pentagonal Cp ligands was shown. In the case of the Be derivative at first a structure containing one symmetrical and one diene-type Cp ligand was proposed, since it accounted for the observed dipole moment. Surprisingly for Cp_2Be recently the space group C_{2h}^5 has been found (101) as earlier observed for Cp_2Fe .

TABLE XXVII
TYPICAL BANDS FOR PENTAGONAL SYMMETRIC C_5H_5 LIGANDS

Frequency no.	Frequency range (cm^{-1})	Number of bands	Intensity
1	3012-3115	1	m-s
2	1400-1447	1	m-s
3	1097-1126	1	vw-s
4	988-1017	1	s
5	712- 850	1	s-vs

For the tetracyclopentadienyls of Zr, Hf, Nb, Ta, and Mo the infrared spectra show pentagonally bound and diene cyclopentadienyl ligands. The number of each type cannot yet be clearly determined. Quantitative intensity measurements might provide useful information.

VIII

EXPERIMENTAL RESULTS FOR SIX-MEMBERED RINGS

A. Benzene

The vibrational spectrum of benzene has been discussed many times (29, 102–108) and, except for the frequencies of representation B_{2u} , has been assigned unequivocally (109, 110). Interestingly the symmetry D_{6h} was not immediately established from the vibrational spectrum, since the latter exhibits some peculiarities, such as Fermi resonance of combination bands, etc. This was not at first recognized. From the spectral predictions of Table XXVIII we now know that four infrared- and seven Raman-active n.v. should be observed for the planar D_{6h} molecule.

TABLE XXVIII

SPECTRAL EXPECTATIONS FOR C_6H_6 WITH D_{6h} SYMMETRY

D_{6h}	C_6H_6	C_6	C—H	Activity
A_{1g}	2	1 (1)	1 (2)	p, ia
A_{1u}	—	—	—	fb, ia
A_{2g}	1	—	1 (3)	fb, ia
A_{2u}	1	—	1 (11)	fb, M_z
B_{1g}	—	—	—	fb, ia
B_{1u}	2	1 (12)	1 (13)	fb, ia
B_{2g}	2	1 (4)	1 (5)	fb, ia
B_{2u}	2	1 (14)	1 (15)	fb, ia
E_g^+	4	2 (6, 8)	2 (7, 9)	dp, ia
E_u^+	2	1 (16)	1 (17)	fb, ia
E_g^-	1	—	1 (10)	dp, ia
E_u^-	3	1 (19)	2 (18, 20)	fb, M_{xy}

The vibrations are numbered as done elsewhere (29). The 20 normal frequencies of Table XXIX were determined for the gaseous and the liquid phase (111).

TABLE XXIX
NORMAL FREQUENCIES OF C_6H_6 (D_{6h})

Frequency ^a		Irreducible representation	Frequency no.	Activity
Gaseous phase	Liquid phase			
3073	3062	A_{1g}	2	p, ia
3064	3053	E_u^-	20	fb, M_{xy}
3057	3048	B_{1u}	13	fb, ia
3056	3048	E_g^+	7	dp, ia
1599	1594	E_g^+	8	dp, ia
1482	1479	E_u^-	19	fb, M_{xy}
1350	1346	A_{2g}	3	fb, ia
1309	1309	B_{2u}	14	fb, ia
1178	1178	E_g^+	9	dp, ia
1146	1146	B_{2u}	15	fb, ia
1037	1035	E_u^-	18	fb, M_{xy}
1010	1010	B_{1u}	12	fb, ia
993	993	A_{1g}	1	p, ia
990	991	B_{2g}	5	fb, ia
967	969	E_u^+	17	fb, ia
846	850	E_g^-	10	dp, ia
707	707	B_{2g}	4	fb, ia
673	675	A_{2u}	11	fb, M_z
606	606	E_g^+	6	dp, ia
398	404	E_u^+	16	fb, ia

^aFrequencies in cm^{-1}

B. Benzene-Metal Complexes

The synthesis of dibenzenechromium, $(C_6H_6)_2Cr$, and benzenechromium tricarbonyl, $C_6H_6Cr(CO)_3$, extended the results obtained for cyclopentadienyls to benzene systems (8). However, the number of known "six-atom carbon ring" complexes does not approach that of those of the five-membered cyclopentadienyl ring system. The theoretical approach to the bonding in this type of complex used by Ruch (112) discussed the possibility of

trigonally distorted benzene ligands. An analysis of the vibrational spectrum of $(C_6H_6)_2Cr$ therefore raised much interest. In early 1959 the first results of infrared studies on polycrystalline dibenzenechromium- H_6 and $-D_6$ were interpreted in terms of a D_{3d} symmetry for the entire molecule (113). The structure of the ligand rings could not be established, beyond the fact that they must be trigonally distorted, as was later found in the second X-ray diffraction study of $(C_6H_6)_2Cr$ (114).

1. *Dibenzene-Metal Complexes*

The most detailed investigation and the only one which combines both infrared and Raman spectra is mainly concerned with the dibenzenechromium cation, $[(C_6H_6)_2Cr]^+$ (38). However, the infrared spectra of uncharged complexes were also given. Due to the dark color and low solubility of dibenzenechromium(O), as well as the similarity of solvent absorptions, only the inner vibrations of the complex framework were observable in the Raman spectrum of its benzene solution. While in this work (38) the partial vapor phase infrared spectrum of $(C_6H_6)_2Cr$ was also reported, another study described the infrared spectrum of the uncharged complex at $-180^\circ C$. The main purpose of this paper (115) was the comparison of the infrared spectrum of dibenzenechromium and benzene with that of ferrocene.

The space available does not permit giving more than an outline of the procedure used in analysis of the vibrational spectra, and the most important results. As already mentioned there are two principal ways of considering the spectra of metal complexes of aromatic ring systems, depending on the assumption of perceptible or of negligible coupling between ligand vibrations through the central atom. Since the complete vibrational spectrum is known only for the dibenzenechromium(I) cation the first method has been employed for this case, while the second method has been used for interpreting the infrared spectra of benzenechromium tricarbonyl- H_6 and $-D_6$ (44). Again, as in the case of the dicyclopentadienyl complexes, it is advisable to consider the frequencies of the ligands separately from those of the molecular framework. Significant structures for the single ligands in these complexes are D_{6h} and C_{6v} , as well as D_{3h} , D_{3d} , and C_{3v} . According to the method, ligand symmetries must be considered only within the symmetry of the entire complex. Dibenzene-metal complexes can have the point groups D_{6h} , D_{6d} , C_{6v} , D_{3d} , or C_{3v} . However, the center of inversion [established by X-ray diffraction (116, 114)] excludes all structures but D_{6h} and

D_{3d} . Due to the possible ligand structures the vibrational spectrum can only confirm the symmetry of the entire complex, if the "strong" coupling case is assumed. Figure 9 shows three possible structures for a dibenzene-metal complex. In Fig. 9a the entire complex as well as the ligands have D_{6h}

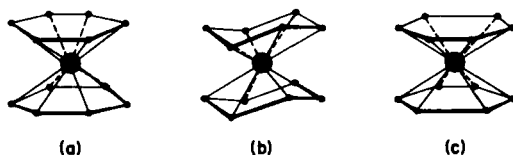


FIG. 9. Possible structures of a dibenzene-metal complex.

symmetry, in Fig. 9b both belong to D_{3d} , while in Fig. 9c the complex has point group D_{3d} and the single ligand D_{3h} . The spectral predictions are given in Table XXX for the two possible symmetries D_{6h} and D_{3d} .

TABLE XXX

GENERAL SELECTION RULES FOR DIBENZENCHROMIUM POINT GROUPS D_{6h} AND D_{3d}

	IR-active	Raman-active	fb, ia	Pseudo-coincidences
D_{6h}				
Ligand vibrations	7	13	20	7
Skeletal vibrations	3	2	1	—
Total number of vibrations	10	15	21	7
D_{3d}				
Ligand vibrations	17	17	6	17
Skeletal vibrations	3	2	1	—
Total number of vibrations	20	19	7	17

Due to the center of inversion, the rule of mutual exclusion must apply to the vibration of the complexes. However, since the vibrations of the ring ligands should have only weak coupling between in-phase and out-of-phase modes, for these vibrations frequency splittings might be expected. These can be rather small, so that "pseudo-coincidences" should occur. Thus experimental criteria for distinguishing between D_{6h} and D_{3d} are (a) the number of observed normal vibrations, (b) the number of pseudo-coincidences, and (c) the number of n.v. appearing *only* in the Raman spectrum.

a. *Skeletal or Inner Vibrations of the Complexes.* Spectral selection rules show that for D_{6h} and D_{3d} symmetries always the same number and types of n.v. of the molecular framework are infrared- and Raman-active. Therefore, we can summarize all the inner vibrations of the known dibenzene-metal complexes in Table XXXI without assuming the correct molecular symmetry.

TABLE XXXI
SKELETAL VIBRATIONS OF DIBENZENE-METAL COMPLEXES

Type of vibration	Symm. stretch	Torsion	Asymm. stretch	Symm. ring tilt	Asymm. ring tilt	Ring-M-ring deformation
Irreducible representation (D_{6h})	A_{1g}	A_{1u}	A_{2u}	E_g^-	E_u^-	E_u^-
Frequency no. ^a	21	22	23	24	25	26
Activity	p, ia	fb, ia	fb, M_z	dp, ia	fb, M_{xy}	fb, M_{xy}
$(C_6H_6)_2Cr$	270 ^b	(305) ^c	459	332	490	(140)
$[(C_6H_6)_2Cr]I$	279	(303)	415	333	466	(144)
$(C_6D_6)_2Cr$	—	—	423	—	479	—
$(C_6H_6)_2Mo$	—	—	362	—	424	—
$[(C_6H_6)_2Mo]I$	—	—	333	—	410	—
$(C_6H_6)_2W$	—	—	331	—	386	—
$[(C_6H_6)_2W]I$	—	—	306	—	378	—
$(C_6H_6)_2V$	—	—	424	—	470	—
$[(C_6H_6)_2Tc]PF_6$	—	—	358	—	431	—
$[(C_6H_6)_2Re]PF_6$	—	—	336	—	396	—

^a See ref. (38).

^b Frequencies in cm^{-1} .

^c Values in parentheses are determined from combination bands.

The assignment of the n.v. for $(C_6H_6)_2Cr$ and its cation are established (38), while the n.v. of the other complexes were assigned by analogy. Snyder has reported essentially the same values for dibenzene-chromium (115).

b. *Ligand Vibrations.* The formal treatment of this problem leads to the results given in Table XXXII.

The approximate vibrational modes of the ligands can be derived from the corresponding ones of the free benzene molecule (106, 111), assuming that the complex contains two rings mechanically coupled through the

metal. This leads to a situation well-known elsewhere, the appearance of in-phase (Gleichtakt) and out-of-phase (Gegentakt) modes, having their phases shifted by 180° . Figure 10 shows this for the case of the totally symmetric ring breathing. The procedure is illustrated in Table XXXIII (38).

TABLE XXXII

GENERAL SELECTION RULES FOR LIGAND VIBRATIONS OF DIBENZENE-METAL COMPLEXES
WITH D_{6h} AND D_{3d} SYMMETRY^a

	IR-active	Raman-active	fb, ia	Pseudo-coincidences
D_{6h}				
CC Skeleton vibrations	2	5	9	2
CH Vibrations	5	8	11	5
Total number of vibrations	7	13	20	7
D_{3d}				
CC Skeleton vibrations	7	7	2	7
CH Vibrations	10	10	4	10
Total number of vibrations	17	17	6	17

^a Degenerate vibrations are counted only once.

Since the seven n.v. assignable to D_{6h} symmetry of the entire molecule or a C_{6v} local symmetry for the ligand rings must appear in six- or threefold symmetry, we can assign the corresponding bands for all known dibenzene-metal complexes. Table XXXIV gives this data.

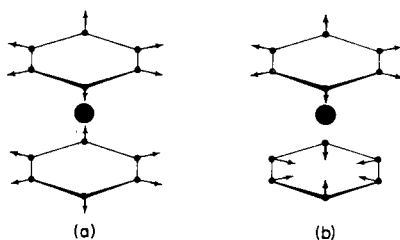


FIG. 10. In-phase (a) and out-of-phase (b) totally symmetric ring breathing.

TABLE XXXIII
 CORRELATION OF BENZENE FREQUENCIES

π -Complexed benzene with (D_{6h}) symmetry		π -Complexed benzene with (D_{3d}) symmetry		
Out-of-phase	In-phase	Benzene D_{3d}	In-phase	Out-of-phase
$A_{2u}(\text{fb}, M_z)$	$A_{1g}(\text{p}, \text{ia})$	$A_{1g}(\text{p}, \text{ia})$	$A_{1g}(\text{p}, \text{ia})$	$A_{2u}(\text{fb}, M_z)$
$A_{1u}(\text{fb}, \text{ia})$	$A_{2g}(\text{fb}, \text{ia})$	$A_{2g}(\text{fb}, \text{ia})$	$A_{2g}(\text{fb}, \text{ia})$	$A_{1u}(\text{fb}, \text{ia})$
$A_{1g}(\text{p}, \text{ia})$	$A_{2u}(\text{fb}, M_z)$	$A_{2u}(\text{fb}, M_z)$	$A_{2u}(\text{fb}, M_z)$	$A_{1g}(\text{p}, \text{ia})$
$B_{2g}(\text{fb}, \text{ia})$	$B_{1u}(\text{fb}, \text{ia})$	$B_{1u}(\text{fb}, \text{ia})$	$A_{2u}(\text{fb}, M_z)$	$A_{1g}(\text{p}, \text{ia})$
$B_{1u}(\text{fb}, \text{ia})$	$B_{2g}(\text{fb}, \text{ia})$	$B_{2g}(\text{fb}, \text{ia})$	$A_{1g}(\text{p}, \text{ia})$	$A_{2u}(\text{fb}, M_z)$
$B_{1g}(\text{fb}, \text{ia})$	$B_{2u}(\text{fb}, \text{ia})$	$B_{2u}(\text{fb}, \text{ia})$	$A_{1u}(\text{fb}, \text{ia})$	$A_{2g}(\text{fb}, \text{ia})$
$E_u^+(\text{fb}, \text{ia})$	$E_g^+(\text{dp}, \text{ia})$	$E_g^+(\text{dp}, \text{ia})$	$E_g(\text{dp}, \text{ia})$	$E_u(\text{fb}, M_{xy})$
$E_g^+(\text{dp}, \text{ia})$	$E_u^+(\text{fb}, \text{ia})$	$E_u^+(\text{fb}, \text{ia})$	$E_u(\text{fb}, M_{xy})$	$E_g(\text{dp}, \text{ia})$
$E_u^-(\text{fb}, M_{xy})$	$E_g^-(\text{dp}, \text{ia})$	$E_g^-(\text{dp}, \text{ia})$	$E_g(\text{dp}, \text{ia})$	$E_u(\text{fb}, M_{xy})$
$E_g^-(\text{dp}, \text{ia})$	$E_u^-(\text{fb}, M_{xy})$	$E_u^-(\text{fb}, M_{xy})$	$E_u(\text{fb}, M_{xy})$	$E_g(\text{dp}, \text{ia})$

 TABLE XXXIV
 INFRARED-ACTIVE NORMAL VIBRATIONS OF π - C_6H_6 IN BENZENE-METAL COMPLEXES^a

Compound	Frequency no. ^b						
	2	20	19	18	1	10	11
$(C_6H_6)_2Cr$	3037	—	1426	999	971	833	794
$[(C_6H_6)_2Cr]^+$	3040	—	1430	1000	972	857	795
$(C_6D_6)_2Cr$	2252	2212	1271	802	928	669	735
$(C_6H_6)_2Mo$	3030	2916	1425	995	966	811	773
$(C_6H_6)_2W$	3012	2898	1412	985	963	882	798
$(C_6H_6)_2V$, cubic	3058	—	1416	985	959	818	739
$(C_6H_6)_2V$, monoclinic	3062	2928	1415	988	957	818	742
$[(C_6H_6)_2Tc]^+$	3096	2933	1443	978	919	—	PF_6^- —
$[(C_6H_6)_2Re]^+$	3086	2941	1437	979	923	—	PF_6^- —
$CpCrC_6H_6$	3061	—	1410	981	956	838	779
$CpMnC_6H_6$	3049	2916	1427	977	—	870	808
$[CpCoC_6H_6]PF_6$	3096	—	1449	986	957	—	PF_6^- —
$[CpRhC_6H_6]PF_6$, or BF_4^- salt	3125	2933	1449	981	957	887	795

^a Frequencies in cm^{-1} .^b According to Wilson *et al.* (29).

In addition the bands of the benzene ligands in a few cyclopentadienyl metal-benzene complexes are listed. For Tc, Re, and Co complexes the observation of the ν_{CH} near 800 cm^{-1} is masked by the P—F and B—F absorptions of the anions.

c. *Distinction Between Six- and Threefold Symmetry.* For $[(\text{C}_6\text{H}_6)_2\text{Cr}]\text{I}$ the number of n.v. of pseudo-coincidences, and the number of n.v. appearing only in the Raman spectrum unequivocally confirm the D_{6h} symmetry of the entire complex. In the range of 2750 to 3500 cm^{-1} for both the cation as well as the uncharged dibenzenechromium too few normal vibrations are observed for either D_{6h} or D_{3d} symmetry. Therefore, ν_{CH} cannot be used to confirm the correct symmetry. Also, between 1250 and 2750 cm^{-1} two n.v. should be observed for both point groups, so that no decision is possible. However, in the range from about 950 to 1250 cm^{-1} a perceptible increase in the number of n.v. takes place. Here for the two symmetries D_{6h} and D_{3d} two and five infrared-active n.v. are to be expected, respectively. Indeed, there are four detectable bands for $[(\text{C}_6\text{H}_6)_2\text{Cr}]\text{I}$ and nine for $(\text{C}_6\text{H}_6)_2\text{Cr}$. Thus, a lowering of symmetry can be inferred. The best agreement with the expected types of bands is obtained by assuming D_{3d} symmetry for the entire molecule and D_{3h} for a single ligand (in this case considering the local symmetry of the ring). Summarizing, one finds bands at *ca.* 971 , 999 , 1012 , 1022 , 1069 , 1137 , and 1142 cm^{-1} , being typical for threefold distortion of the ring ligands, compared with absorptions of 975 , 1000 , and 1137 cm^{-1} for the cation. The " 1012 cm^{-1} band" is observed at -180°C in the crystalline state with especially high intensity at 1014 cm^{-1} .

A recently repeated X-ray analysis of $(\text{C}_6\text{H}_6)_2\text{Cr}$ indicated the differences of the alternating C—C bond lengths of the previously found (114) "Kekulé" structure in the ring ligands to be less than 0.2 \AA , with the mean value being about 1.40 \AA . Therefore, only a slight degradation, if any, of sixfold symmetry was inferred (116a).

For practically all other dibenzene-metal complexes threefold distortion of the ring ligands cannot be established. Quite often objections have been raised to the experimentally determined distortion of the rings, since simple molecular orbital considerations do not predict deformation. The threefold symmetry was assumed to originate from the threefold axes of symmetry of the cubic system in which dibenzenechromium crystallizes. However, quite recently (117), a cubic modification of $(\text{C}_6\text{H}_6)_2\text{V}$ has been found and carefully investigated, in addition to the previously known monoclinic one. Both modifications were found to exhibit virtually identical infrared spectra,

hence the influence of the cubic crystal field can be neglected for $(C_6H_6)_2Cr$, also. Furthermore, both spectra prove the existence of D_{6h} symmetry for the vanadium complex.

2. Benzene-Metal Carbonyls

Transition metal complexes having only benzene and carbon monoxide as ligands are tricarbonyls, with the exception of the cation $[(C_6H_6)_3Co_3(CO)_2]^+$. The infrared spectra of the benzene-metal carbonyls were usually reported at the time their synthesis was described. As far as the vibrational frequencies of the ring ligands are concerned they show some additional bands as the main difference from the dibenzene-metal complexes. For $C_6H_6M(CO)_3$ application of local symmetry is straightforward, and so this method has been employed for interpreting the infrared spectra of $C_6H_6Cr(CO)_3$ and $C_6H_6Mo(CO)_3$ as well as their perdeuterated derivatives (44, 118). Clearly a threefold distortion of the ligand rings can be deduced from the spectra for both complexes.

Table XXXV lists the seven infrared-active n.v. assuming metal-ring local C_{6v} symmetry. In addition to these bands in the chromium and molybdenum complexes eight other n.v. can be assigned according to C_{3v} local symmetry of the ligand rings. The other benzene-metal carbonyls have yet to be studied more thoroughly in order to decide on the exact symmetry of the rings.

TABLE XXXV

INFRARED-ACTIVE NORMAL VIBRATIONS OF π - C_6H_6 IN BENZENE-METAL CARBONYLS

Compound	Frequency no. ^a						
	2	20	19	18	1	10	11
$C_6H_6Cr(CO)_3$	3086	2931	1445	1016	978	965	784
$C_6D_6Cr(CO)_3$	2285	2215	1292	806	930	791	702
$C_6H_6Mo(CO)_3$	3106	2933	1439	1009	1005	967	763
$C_6D_6Mo(CO)_3$	2342	2310	1285	902	973	816	696
$C_6H_6W(CO)_3$	—	—	1433	1003	966	891	776
$[C_6H_6Mn(CO)_3]ClO_4$	3086	—	1453	1013	—	827	—
			1433				
$[(C_6H_6)_3Co_3(CO)_2]^+$	3048	—	1445	1008	976	908	793
							776

^a According to Wilson *et al.* (29).

^b Ref.(118a).

3. Other Benzene-Metal Complexes

In addition to the benzene complexes discussed in the previous sections there are a number of other known compounds containing benzene ligands coordinated to metal atoms.

The complex studied first was the addition product of antimony trichloride and benzene (119). Two bands at 1236 and 477 cm^{-1} in the Raman spectrum were assigned to metal-ring vibrations. More recent Raman work (120, 121), as well as infrared studies (122, 123), show definitely that the ring ligand does not retain the original D_{6h} symmetry of the free hydrocarbon. A C_{3v} or even C_{2v} structure seems to account for the observed spectra most plausibly.

The structure of the silver perchlorate complex of benzene, $C_6H_6 \cdot AgClO_4$, has been determined by X-ray diffraction (123a). According to the results the Ag atom is situated approximately above one of the CC bonds of the benzene ring. Nevertheless, the infrared spectrum exhibits remarkably few absorption bands (122) for the established symmetry of the solid complex. However, the infrared spectrum of a polycrystalline sample shows the absence of intense bands near 1000 cm^{-1} , typical of π complexes of benzene with a centrosymmetrical arrangement for the metal atom (123). The low position of the band corresponding to ν_{11} of C_6H_6 at 725 cm^{-1} indicates weak bond strength between the metal and the ring. This is in agreement with the fact that no metal-ligand vibration can be assigned unambiguously in the far infrared. All bands appearing down to about 400 cm^{-1} can be easily attributed to vibrational modes of the ring. Although further studies, for example of the perdeuterated complex, would bring a more exact interpretation of the IR spectrum, it seems possible to assign all 15 n.v. predicted for a structure similar to that originally assumed for the $[C_4H_4Ag]^+$ ion (Fig. 3) with C_{2h} symmetry. The Raman spectrum shows two lines at 215 and 130 cm^{-1} (123b), which certainly originate from a Ag-ligand stretching and tilting mode, respectively. The rule of mutual exclusion is valid for all observed infrared and Raman-active n.v. in good agreement with the C_{2h} symmetry of the complex ion.

Very recently benzene complexes of the general formula $M_2Hg(SCN)_6 \cdot C_6H_6$ ($M = Co, Ni, \text{ or } Cd$) have been studied. Again the symmetry of the ligand ring is lowered from D_{6h} probably to D_{3d} (124).

In contrast to all the above-mentioned compounds, the benzene ring in the clathrate compound $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ has sixfold symmetry, as in the free hydrocarbon (125, 123).

The principle allowing application of the method of local symmetry for interpreting all the vibrational spectra of the compounds discussed in this section is that the positions of the intense normal frequencies of benzene appear only slightly shifted in the complex spectra. This leads to the conclusion that the bonding forces between metals and the benzene ring cannot be very important. They are, however, strong enough to cause a distortion of the rings in some cases. An investigation of the spectra of benzene complexes of Al, Ga, Hg, Co, and other metals is under way (123). Relevant also is the preparation of benzene complexes of the type of $C_6H_6MX_n$ (M, Ti, Nb, etc.) (126), as well as complexes of general formula $[M(C_6H_6)]^{n+}(AlCl_4)_n$ (with M equal to a large variety of main group and transition metals) (127). The determination of their ligand symmetries will yield further information on the theory of bonding in benzene complexes.

4. Ring-Substituted Benzene Complexes

The number of substituted dibenzenechromium homologs is rather small, only alkyl and aryl substituents being known, compared with the number of complexes of substituted cyclopentadienyls (8). It is difficult to suggest a correlation comparable with the "9,10 μ rule" due to the small number of known examples. The only band disappearing from the infrared spectra of all complexes in both rings is the intense symmetric ring breathing vibration which appears at 972 cm^{-1} in $(C_6H_6)_2Cr$. This is surprising, since for the substituted cyclopentadienyls two C—H frequencies disappear. The 972 cm^{-1} band is not observed in bis(methyl benzoate)chromium(O) (128), and it was not reported in the spectrum of benzoic acid (biphenyl)chromium(I)-tetraphenyl borate (129). The esterification of this acid cation with diazomethane affords a methyl benzoate-(biphenyl)chromium cation. In this complex the C=O group has its stretching vibration at 1725 cm^{-1} in contrast to 1704 and 1689 cm^{-1} found in the uncharged mono- and di-substituted dibenzenechromium complexes (130). Since methyl benzoate exhibits this absorption at 1724 cm^{-1} , the complex might be a benzene(biphenyl)-chromium cation with the $COOCH_3$ group in the noncomplexed ring of the biphenyl ligand.

Substituted-benzene-metal tricarbonyls of chromium, molybdenum, and tungsten do not have any intense band in the 900 to 980 cm^{-1} range, while the parent compounds absorb at 902 and 978 cm^{-1} , respectively (131). The IR spectra of hexamethyl-, hexaethyl-, and *meta*-diisopropylbenzene(Mo, W) tricarbonyls show weak to medium intensity bands, probably due to some

substituent vibrations or perhaps due to impurities. Thus for substituted-benzene-metal tricarbonyls a "10, 11 μ rule" can be tentatively suggested.

A study of the infrared spectra of a series of substituted-benzene chromium tricarbonyls has been carried out in order to compare them with the spectra of the free parent hydrocarbons (132). The property that in the infrared spectra of π complexes of aromatic hydrocarbons the ν_{CH} 's show a decrease in intensity in the complex, was confirmed and the shifts of some bands were discussed.

IX

EXPERIMENTAL RESULTS FOR SEVEN-MEMBERED RINGS

A. Tropylium Cation, $(\text{C}_7\text{H}_7)^+$

The vibrational spectrum of the tropylium cation in $(\text{C}_7\text{H}_7)\text{Br}$ was reported and discussed a few years ago (133, 134). In agreement with the theoretical predictions of the Hückel rule, a planar, regular heptagon was found. Table XXXVI shows that four infrared and seven Raman-active n.v. are to be expected. The infrared spectra of several other tropylium salts exhibit remarkably few intense bands, so that the D_{7h} symmetry can be generally accepted.

TABLE XXXVI
SPECTRAL EXPECTATIONS FOR C_7H_7 WITH (D_{7h}) SYMMETRY

D_{7h}	C_7H_7	C_7	C—H	Activity
A'_1	2	1 [ω]	1 [ν]	p, ia
A''_1	—	—	—	fb, ia
A'_2	1	—	1 (δ)	fb, ia
A''_2	1	—	1 [γ]	fb, M_z
E'_1	3	1 [ω]	2 [ν , δ]	fb, M_{xy}
E''_1	1	—	1 [γ]	dp, ia
E'_2	4	2 [ω , Δ]	2 [ν , δ]	dp, ia
E''_2	2	1 [I]	1 [γ]	fb, ia
E'_3	4	2 [ω , Δ]	2 [ν , δ]	fb, ia
E''_3	2	1 [I]	1 [γ]	fb, ia

Table XXXVII lists the frequency assignments for $(C_7H_7)Br$ (134). It should be mentioned, however, that the volatility of tropylium bromide indicates partial covalent bonding between $(C_7H_7)^+$ and Br^- . Therefore, the $(C_7H_7)^+$ frequencies in tropylium bromide cannot be considered characteristic of those of a "purely" ionic system.

TABLE XXXVII
INFRARED- AND RAMAN-ACTIVE NORMAL VIBRATIONS OF $[C_7H_7]Br$

Frequency	Irreducible representation	Type of vibration	Activity
3075	E'_2	CH stretch	Raman
3060	A'_1	CH stretch	Raman
3020	E'_1	CH stretch	IR
1594	E'_2	CC stretch	Raman
1477	E'_1	CC stretch	IR
1210	E'_2	CH deformation (\parallel)	Raman
992	E'_1	CH deformation (\parallel)	IR
868	A'_1	CC stretch	Raman
—	E''_1	CH deformation (\perp)	Raman
633	A''_2	CH deformation (\perp)	IR
433	E'_2	CCC deformation (\parallel)	Raman

B. π - C_7H_7 -Metal Complexes

When in the infrared spectrum of a C_7H_7 compound more than the four n.v. of D_{7h} can be assigned, strong interaction has lowered the symmetry of the ring to at least C_{7v} . This is the case when complex formation occurs. Table XXXVIII shows the spectral expectations for a metal- (C_7H_7) group having C_{7v} symmetry. The first complex of this type to be reported, $(C_7H_7PtBr_2)_2$, exhibits the seven n.v. to be expected for C_{7v} (135). Since frequencies are only shifted slightly from the n.v. of C_7H_7Br , relatively weak complex bonding can be assumed in this case. The other known C_7H_7 complexes were also obtained starting from C_7H_8 (136–138). Since benzene-metal tricarbonyls can be produced by treating the cations $[C_7H_7M(CO)_3]^+$ ($M = Cr, Mo$) with NaC_5H_5 (139), or as decomposition products of these cations, a bicyclic norcaradienyl structure for the C_7H_7 ligands could be considered. However, it is impossible to assign all 36 n.v. expected for the C_s symmetry of such a bicyclic ligand.

TABLE XXXVIII
SPECTRAL EXPECTATIONS FOR $(C_7H_7)M$ WITH (C_{7v}) SYMMETRY

C_{7v}	C_7H_7M	C_7H_7	C_7	C—H	M—Ligand	Activity
A_1	4	3	1 $[\omega]$	2 $[\nu, \gamma]$	Stretch	p, M_z
A_2	1	1	—	1 $[\delta]$	—	fb, ia
E_1	5	4	1 $[\omega]$	3 $[\nu, \delta, \gamma]$	Deformation	dp, M_{xy}
E_2	6	6	3 $[\omega, \Delta, \Gamma]$	3 $[\nu, \delta, \gamma]$	—	dp, ia
E_3	6	6	3 $[\omega, \Delta, \Gamma]$	3 $[\nu, \delta, \gamma]$	—	fb, ia

Table XXXIX lists the seven infrared-active n.v. of five π - C_7H_7 complexes. It can be seen that for seven-membered rings in complexes the same regularity occurs as for five-membered rings, namely, bond strength between metal and ring is increased, if the lowest γ_{CH} is shifted to higher frequencies.

TABLE XXXIX
INFRARED-ACTIVE NORMAL VIBRATIONS OF C_7H_7 -METAL COMPLEXES

Compound	ν_{CH}	ν_{CH}	ω_{CC}	δ_{CH}	γ_{CH}	ω_{CC}	γ_{CH}
$[C_7H_7PtBr_2]_2$	3052	3017	1473	1277	914	839	744
$[C_7H_7Cr(CO)_3]BF_4$	3077	2933	1450	1262	970	864	816
$[C_7H_7Mo(CO)_3]BF_4$	3081	2928	1440	1259	958	861	807
$C_7H_7VC_5H_5$	3068	2941	(1421)	1240	957	851	784
$C_7H_7V(CO)_3$	3021	2933	1431	1244	960	844	785

In the far-infrared region the spectrum of $C_7H_7VC_5H_5$ exhibits only two intense bands. According to a linear three-mass XYZ model with rigid ring ligands metal–ring stretching vibrations for each ring, as well as at least one ring tilting vibration, should be observed. The n.v. of the cyclopentadienyl ligand can be identified by the absorptions at 1421, 1108, 1012, 1003, 816, 802, and 432 cm^{-1} .

X

EXPERIMENTAL RESULTS FOR EIGHT-MEMBERED RINGS

The last member in the C_nH_n series is cyclooctatetraene (COT). Since COT itself is not a planar $(4n+2)$ π electron system (140–142), our discussion can be restricted to the $[C_8H_8]^{2-}$ anion and to COT complexes.

A. Cyclooctatetraenyl Anion, $(C_8H_8)^{2-}$

Following the D_{8h} symmetry of all uncomplexed C_nH_n hydrocarbons discussed in this chapter, spectral expectations again predict only four infrared- and seven Raman-active normal vibrations for $C_8H_8^{2-}$ (Table XL). Due to

TABLE XL
SPECTRAL EXPECTATIONS FOR $C_8H_8^{2-}$ WITH D_{8h}

D_{8h}	C_8H_8	C_8	C—H	Activity
A_{1g}	2	1 [ω]	1 [ν]	p, ia
A_{1u}	—	—	—	fb, ia
A_{2g}	1	—	1 [δ]	dp, ia
A_{2u}	1	—	1 [γ]	fb, M_z
B_{1g}	—	—	—	fb, ia
B_{1u}	2	1 [Δ]	1 [ν]	fb, ia
B_{2g}	2	1 [Γ]	1 [γ]	fb, ia
B_{2u}	2	1 [ω]	1 [δ]	fb, ia
E_{1g}	1	—	1 [γ]	dp, ia
E_{1u}	3	1 [ω]	2 [ν , δ]	fb, M_{xy}
E_{2g}	4	2 [ω , Δ]	2 [ν , δ]	dp, ia
E_{2u}	2	1 [Γ]	1 [γ]	fb, ia
E_{3g}	4	2 [ω , Δ]	2 [ν , δ]	dp, ia
E_{3u}	2	1 [Γ]	1 [γ]	fb, ia

the extreme air sensitivity and the yellow color of solutions of $K_2[C_8H_8]$ it has not yet been possible to obtain a Raman spectrum of this potassium salt. Therefore, in Table XLI only the four infrared n.v. are compared with the corresponding n.v. of KC_5H_5 , C_6H_6 , and C_7H_7Br . The relatively small number of intense bands, only three, for this 16-atom anion proves the planar D_{8h} structure (143, 144).

TABLE XLI
INFRARED-ACTIVE NORMAL VIBRATIONS OF C_5H_5K , C_6H_6 , C_7H_7Br , AND $C_8H_8K_2^a$

Type of vibration	C_5H_5K	C_6H_6	C_7H_7Br	$C_8H_8K_2$
CH stretch (E'_1)(E_{1u})	3021	3064	3020	2994
CC stretch (E'_1)(E_{1u})	1442	1482	1477	1431
CH deformation (\parallel) (E'_1)(E_{1u})	1008	1037	992	880
CH deformation (\perp) (A''_2)(A_{2u})	701	673	633	684

^a Frequencies in cm^{-1} .

As mentioned previously, for cyclopentadienyl absorptions negative charge on the ring seems to exert a strong influence on band positions. For both anionic systems the C—C stretching vibrations are at the highest, and the C—H out-of-plane deformations at the lowest positions. This is remarkable especially with respect to the ω_{CC} , since in $C_5H_5^-$ and $[C_8H_8]^{2-}$ the strength of the C—C bonds is obviously lowered, if one assumes approximately equal bond length in all four C_nH_n systems with $n = 5, 6, 7$, or 8. This is in agreement with the chemical behavior, for example, air sensitivity. The C—H in-plane deformations seem to depend on the ring strain, since there is a decrease in frequencies from C_6H_6 (1037 cm^{-1}) to $C_8H_8^{2-}$ (880 cm^{-1}).

B. π - C_8H_8 -Metal Complexes

For cyclooctatetraene complexes only a few infrared spectroscopic studies have been reported. Three COT complexes have been investigated by X-ray diffraction. Consequently in the following section two types of complex will be distinguished: (a) complexes with known structure in the *crystalline* state, and (b) those for which infrared spectra provides the main evidence for a particular structure.

1. Cyclooctatetraene Complexes with Structures Determined by X-Ray Analysis

The compound $C_8H_8 \cdot AgNO_3$ was found to have the hydrocarbon in the tub form (144a), as found in free C_8H_8 (142). In the infrared spectrum no bands assignable to free C=C bonds occur, and approximately 20 bands can be assigned to n.v. (144). This makes a tub configuration with two Ag^+ ions linked to both sides of the "tub" the most plausible structure. Obviously, all double bonds are involved in rather weak complex bonding. Since no metal–ring vibrations are observed in the far-infrared, weak bonding can be assumed.

X-ray studies on crystalline $C_8H_8Fe(CO)_3$ established a structure with six C atoms in a plane and two neighbouring ones tilted out of this plane. These two are part of a "butadiene" fragment of the molecule which undergoes complex formation with the $Fe(CO)_3$ group (145, 146). The infrared spectrum has been discussed (144). The absence of an intense band due to stretching of conjugated C=C bonds cannot be readily explained. Therefore, participation of all C=C bonds in complex bonding was inferred. However, the similarity of the IR spectra in the solid and the dissolved state seems

to prove that the structure with low symmetry produces the observed single proton resonance signal (146, 147). Previously, a regular octagonal C_8H_8 ring in $C_8H_8Fe(CO)_3$ had been postulated from the infrared spectrum (148, 149).

For $C_8H_8[Fe(CO)_3]_2$ X-ray analysis showed a C_8H_8 ring in "chair" form, the two butadiene parts of which are each bonded to a $Fe(CO)_3$ group (150). The infrared spectrum exhibits both with respect to number and to position the 21 expected n.v. (144). A remarkable similarity to the spectra of butadiene-metal complexes can be observed near 7 to 8 μ .

2. Other C_8H_8 π Complexes

The infrared spectra of $C_8H_8PtI_2$ and $C_8H_8PdCl_2$ also show no bands due to free $C=C$ bonds (144). The large frequency shifts suggest rather stable metal-ring bonds (151). Another type of platinum compounds with general formula $R_2PtC_8H_8PtR_2$ has been described (152). A strong band was observed at 1352 cm^{-1} , characteristic of platinum complexes containing cyclooctatetraene as a bridging unit or as a chelated olefin. In addition the 800 cm^{-1} band shows a remarkable decrease in intensity compared with that of the same band in $C_8H_8PtI_2$.

Two known cobalt complexes of cyclooctatetraene are of the type $C_8H_8(CoC_5H_5)_n$, with $n = 1$ or 2. In the mononuclear complex COT acts as a 1,5-diene with the eight-membered hydrocarbon in the tub configuration (153, 154), while the binuclear complex probably has a central C_8H_8 ligand with a plane tetragonal structure (147, 154).

Recently the two corresponding rhodium homologs have been obtained (155, 156). By NMR measurements the COT ligands were found to retain their tub configuration. The existence of other C_8H_8 metal complexes has been claimed, but no vibrational spectra have been reported.

XI

SOME QUANTITIES DERIVED FROM VIBRATIONAL SPECTRA

In principle a complete normal coordinate analysis of a molecule is possible. However, in general except for molecules with only few atoms the procedure will be too complicated. Therefore, only three complexes Cp_2Fe (17), Cp_2Ru (17, 157), and Cp_2Mg (62) have been treated in this extensive

way. Only with ruthenocene were the metal-to-ring bonds included into the calculations (157); the other studies were restricted to the ligand vibrations.

A very important property for the preparative as well as the theoretical chemist is the strength of the metal-to-ring bonds in a complex. Use of the harmonic oscillator equation

$$(5.89 \times 10^{-2}) \nu^2 \mu = f \quad (1)$$

in which f = force constant, ν = the stretching frequency (cm^{-1}), and μ = the reduced mass $(m_1 \cdot m_2)/(m_1 + m_2)$ of the atoms m_1 and m_2 (in relative atomic weight units) connected by the particular bond can give a clue to the magnitude of the bond strength (24, 25). A slightly more exact result is obtained when for linear YXY molecules the asymmetric X—Y stretching vibration is used (24).

$$(5.89 \times 10^{-2}) \nu_{\text{asym}} = \left(1 + \frac{2m_Y}{m_X}\right) \frac{f}{m_X} \quad (2)$$

If all three n.v. of a YXY molecule or model are known a more general force field can be applied to lead to the equations:

$$(5.89 \times 10^{-2}) \nu_1^2 = \frac{f_1 + f_{12}}{m_Y} \quad (3)$$

$$(5.89 \times 10^{-2}) \nu_2^2 = 2 \left(1 + \frac{2m_Y}{m_X}\right) \frac{1}{m_Y} \frac{f}{l^2} \quad (4)$$

$$(5.89 \times 10^{-2}) \nu_3^2 = \left(1 + \frac{2m_Y}{m_X}\right) \frac{f_1 - f_{12}}{m_Y} \quad (5)$$

For a nonlinear YXY molecule the angle 2α between the two YX bonds has to be considered, so that Eq. (2) is amended to

$$(5.89 \times 10^{-2}) \nu_{\text{asym}} = \left(1 + \frac{2m_Y}{m_X} \sin^2 \alpha\right) \frac{f}{m_Y} \quad (6)$$

The factor 5.89×10^{-2} (or, more exactly, 5.8894×10^{-2}) contains, besides the quantity $4\pi^2$, all conversion factors, so that the normal vibrations can be inserted in the equations in wave numbers (cm^{-1}) instead of wavelengths, with the atomic masses in relative units. Force constants (f) are obtained from the equations in dyne/cm. They will have the order of magnitude 10^5 dyne/cm. It is, however, usual to change to mdyne/Å by omitting the factor 10^5 .

For linear dicyclopentadienyls the results in Table XLII can be deduced from Eq. (2). It is interesting to compare the calculated f -values with the ω_{CC} and γ_{CH} of the ring ligands and with the deviation of the electronic structure of the metal from a filled inert gas shell. There is a clear relationship between electronic configuration and (symmetry) force constants. In addition, the values of γ_{CH} are lowest for complexes not having filled inert gas shells.

TABLE XLII
ESTIMATED SYMMETRY FORCE CONSTANTS FOR FERROCENE-LIKE MOLECULES

Compound	Asymm. stretch	f	ω_{CC}	γ_{CH}	Deviation from inert gas configuration (electrons)
Cp_2Os	353	2.8	1400	823	0
Cp_2Ru	379	2.4	1410	821	0
Cp_2Fe	478	2.7	1408	814	0
$[Cp_2Fe]^+$	423	2.0	1412	817	-1
Cp_2Co	355	1.5	1412	778	+1
$[Cp_2Co]^+$	461	2.5	1414	820	0
Cp_2Ni	355	1.5	1421	772	+2
Cp_2Cr	408	1.6	1404	766	-2
Cp_2V	379	1.5	1425	774	-3
Cp_2Zn	345	1.5	1410	760	Complete 3d shell
Cp_2Mg	439	1.2	1428	758	0

By using Raman data (17, 62) as well as the infrared values from Eqs. (3-5) a less approximate picture can be obtained. [In Table XLIII, for Cp_2Mg , obviously the symmetric Mg ring stretching frequency can be assigned at 191 cm^{-1} (62)].

TABLE XLIII
STRETCHING, INTERACTION, AND DEFORMATION FORCE CONSTANTS

	f_1	f_{12}	f_8/l^2	f (from Eq. 2)
Cp_2Ru	3.20	0.88	0.29	2.4
Cp_2Fe	3.11	0.48	0.66	2.7
Cp_2Ni	1.68	0.18	0.09	1.5
Cp_2Mg	1.83	0.19	0.54	1.2

According to Table XLIII a higher f value is obtained for Cp_2Ru than for Cp_2Fe , in agreement with chemical evidence. The high interaction constant f_{12} for ruthenocene can be perhaps understood, since Cp_2Ru has D_{5h} symmetry, whereas ferrocene belongs to the point group D_{5d} . The eclipsed position of the ligand rings in Cp_2Ru seems to permit stronger coupling of ring vibrations.

The series of dibenzene-metal complexes can be treated similarly. Table XLIV lists the asymmetric metal-ring stretching frequencies and the f

TABLE XLIV

ESTIMATED SYMMETRY FORCE CONSTANTS OF DIBENZENE-METAL COMPLEXES

Metal and oxidation state	Asymm. metal-ring stretch (cm^{-1})	Symmetry force constants from		Deviation from inert gas config. (electrons)
		Eq. 1	Eq. 2	
Cr°	459	3.88	2.43	0
$\text{Cr}^\circ\text{-}d_{12}$	423	3.39	2.32	0
Cr^+	415	3.16	1.98	-1
Mo°	362	3.32	2.29	0
Mo^+	333	2.81	1.95	-1
W°	331	3.53	2.72	0
W^+	306	3.02	2.33	-1
V°	424	3.26	2.24	-1
Tc^+	358	3.28	2.28	0
Re^+	336	3.66	2.78	0

values obtained by using Eqs. (1) and (2). Deviation from the filled inert gas shell again results in a decrease of the force constants. Dibenzene-chromium as well as $(\text{C}_6\text{H}_6)\text{Cr}^+$ (36) can be discussed in terms of the more general force field. This leads to the values

$$(\text{C}_6\text{H}_6)_2\text{Cr}: \quad f_1 = 2.89 \quad f_{12} = 0.47 \quad f_{\delta_{12}} = 0.113 \text{ mdyne/\AA}$$

$$[(\text{C}_6\text{H}_6)_2\text{Cr}]\text{I}: \quad f_1 = 2.78 \quad f_{12} = 0.80 \quad f_{\delta_{12}} = 0.119 \text{ mdyne/\AA}$$

Analysis of the combination bands makes a value of 303 cm^{-1} probable for the ring torsion of the dibenzenechromium cation. Accepting the rather gross approximation of treating the complex cation as a molecule of two equal parts without the central metal, one can use the harmonic oscillator

equation. From the molecular dimensions a rotational constant $A = 1.92 \text{ cm}^{-1}$ is obtained and hence a value for the potential barrier of the order of 1 kcal/mole. For ethane a value of 2.875 kcal/mole is found. Thus the "result" for $(C_6H_6)_2Cr^+$ should at least allow the conclusion that there is essentially no hindrance to rotation around the molecular axis.

In the course of a discussion of the CH stretching vibrations of C_5H_5Tl the relation between the intensities (I) of the A_1 and E vibrations was given as

$$\frac{I(A_1)}{I(E)} = \frac{1}{2} \tan^2 \alpha \quad (7)$$

Since when $\alpha = 18^\circ$ and $\alpha = 27^\circ$ this value is 0.05 and 0.1, respectively, it can be understood that very often only the E-CH stretching vibration is observed for the complexes.

Thermodynamic functions have been determined for Cp_2Fe , Cp_2Ru , and Cp_2Ni (158), as well as for $C_6H_6 \cdot 2SbCl_3$ and $C_6H_6 \cdot AgClO_4$ (122). The thermodynamic functions C_p° and S° for the cyclopentadienyls were found to be considerably lower than for most organometallic compounds of comparable molecular weight. This result agrees with the stability and high symmetry of the complexes (158).

REFERENCES

1. W. C. Zeise, *Pogg. Ann.* **9**, 632 (1827).
2. S. A. Miller, J. A. Tebbboth, and J. F. Tremaine, *J. Chem. Soc.* p. 632 (1952).
3. T. J. Kealy and P. L. Pauson, *Nature* **168**, 1039 (1951).
4. A. N. Nesmeyanov and E. G. Perevalova, *Usp. Khim.* **27**, 3 (1958).
5. E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.* **1**, 55 (1959).
6. G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.* **1**, 1 (1959).
7. H. H. Zeiss, "Organometallic Chemistry," J. Am. Chem. Soc. Monograph No. 147. Reinhold, New York (1960).
8. E. O. Fischer and H. P. Fritz, *Angew. Chem.* **73**, 353 (1961).
9. C. E. Coffey, *J. Am. Chem. Soc.* **84**, 118 (1962).
10. H. P. Fritz and H. Keller, unpublished results.
11. J. Chatt and R. G. Guy, *Chem. Ind. (London)* p. 212 (1963).
12. P. F. Eiland and R. Pepinsky, *J. Am. Chem. Soc.* **74**, 4971 (1952).
13. E. O. Fischer and W. Pfab, *Z. Naturforsch.* **7b**, 377 (1952).
14. J. D. Dunitz and L. E. Orgel, *Nature* **171**, 121 (1953).
15. L. Kaplan, W. L. Kester, and J. J. Katz, *J. Am. Chem. Soc.* **74**, 5531 (1952).
16. E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.* **21**, 1307 (1953).
17. E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta* **10**, 307 (1958).
18. H. J. Taufen, M. J. Murray, and F. F. Cleveland, *J. Am. Chem. Soc.* **63**, 2500 (1941).
19. H. Stammreich, *Spectrochim. Acta* **8**, 41 (1956).

20. L. J. Bellamy, "The IR-Spectra of Complex Molecules," p. 334. Methuen, London (1958).
21. J. Lecomte, in "Handbuch der Physik" (S. Flügge, ed.), Vol. 26, p. 244. Springer, Vienna, 1958.
22. F. A. Cotton, in "Modern Coordination Chemistry" (J. Lewis and R. G. Wilkins, eds.), p. 301. Interscience, 1960.
23. H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry", Wiley, New York, 1944.
24. G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II. Van Nostrand, Princeton, New Jersey, 1945.
25. K. W. F. Kohlrausch, "Struktur und Eigenschaften der Materie, Ergänzungsband 1931-1937," Vol. 19. Springer, Vienna, 1938.
26. G. M. Barrow, "Introduction to Molecular Spectroscopy," McGraw-Hill, New York, 1962.
27. W. Brügel, "Einführung in die Ultrarotspektroskopie," 2nd ed. Steinkopff, Darmstadt, Germany, 1957.
28. J. Brandmüller and H. Moser, "Einführung in die Ramanspektroskopie," 1st ed. Steinkopff, Darmstadt, Germany, 1962.
29. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations." McGraw-Hill, New York, 1955.
30. G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, p. 256. Van Nostrand, Princeton, New Jersey, 1945.
31. G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, p. 83. Van Nostrand, Princeton, New Jersey, 1945.
32. G. Bor and L. Marko, *Spectrochim. Acta* **16**, 1105 (1960).
33. F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.* p. 1822 (1960).
34. O. S. Mills and G. Robinson, *Proc. Chem. Soc.* p. 156 (1959).
35. R. N. Jones and C. Sandorfy, in "Chemical Applications of Spectroscopy" (W. West, ed.), p. 247 and ff. Interscience, New York, 1956.
36. H. P. Fritz, Habil. Thesis, Univ. Munich, Munich, Germany, 1962.
37. S. Mizushima, in "Handbuch der Physik" (S. Flügge, ed.), Vol. 26, p. 171. Springer, Vienna, 1958.
38. H. P. Fritz, W. Lüttke, H. Stammreich, and R. Forneris, *Spectrochim. Acta* **17**, 1068 (1961).
39. F. A. Cotton and L. T. Reynolds, *J. Am. Chem. Soc.* **80**, 269 (1958).
40. W. K. Winter, B. Curnutte, and S. E. Whitcomb, *Spectrochim. Acta* **15**, 1085 (1959).
41. G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.* **2**, 95 (1956).
42. B. L. Crawford, Jr. and E. B. Wilson, Jr., *J. Chem. Phys.* **9**, 323 (1941).
43. H. Stammreich, *Spectrochim. Acta* **13**, 192 (1958).
44. H. P. Fritz and J. Manchot, *Spectrochim. Acta* **18**, 171 (1962).
45. R. Breslow and H. W. Chang, *J. Am. Chem. Soc.* **83**, 2367 (1961).
46. K. Wiberg and B. J. Nist, *J. Am. Chem. Soc.* **83**, 1226 (1961).
47. D. N. Kursanov, M. E. Volpin, and Y. D. Koreshtshkov, *Zh. Obshch. Khim.* **30**, 2877 (1960).
48. Cf. C. A. Coulson and W. Moffitt, *Phil. Mag.* [7] **40**, 1 (1948).
49. R. P. Dodge and V. Schomaker, *Nature* **186**, 798 (1960).
50. J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta* **45**, 647 (1962).
51. H. P. Fritz, *Z. Naturforsch.* **16b**, 415 (1961).

52. H. P. Fritz, *Rev. Chim. (Bucharest)* (in press).
53. H. P. Fritz, J. F. W. McOmie, and N. Sheppard, *Tetrahedron Letters* **26**, 35 (1960).
54. M. Avram, H. P. Fritz, H. Keller, Gh. Mateescu, J. F. W. McOmie, N. Sheppard, and C. D. Nenitzescu, *Tetrahedron* **19**, 187 (1963).
55. M. Avram, H. P. Fritz, H. Keller, C. G. Kreiter, Gh. Mateescu, J. F. W. McOmie, N. Sheppard, and C. D. Nenitzescu, *Tetrahedron Letters* (in press).
56. J. Thiele, *Ber. Deut. Chem. Ges.* **34**, 71 (1901).
57. H. P. Fritz, *Chem. Ber.* **92**, 780 (1959).
58. H. Stammreich, personal communication.
59. H. P. Fritz and R. Schneider, *Chem. Ber.* **93**, 1171 (1960).
60. A. N. Radionov, D. N. Shigorin, T. Talalaeva, and K. A. Kosheshkov, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk* p. 120 (1958); D. N. Shigorin, *Spectrochim. Acta* **14**, 198 (1959).
61. R. West and W. Glaze, *J. Am. Chem. Soc.* **83**, 3580 (1961).
62. E. R. Lippincott, J. Xavier, and D. Steele, *J. Am. Chem. Soc.* **83**, 2262 (1961).
63. H. P. Fritz and E. O. Fischer, *J. Chem. Soc.* p. 547 (1961).
64. D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.* **83**, 4474 (1961).
- 64a. G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.* **77**, 3421 (1955).
65. M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 4854 (1961).
66. F. A. Cotton, H. Stammreich, and G. Wilkinson, *J. Inorg. Nucl. Chem.* **9**, 3 (1959).
67. A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.* p. 3172 (1961).
68. R. D. Fischer, Ph.D. thesis, Univ. Munich, Munich, Germany, 1961.
69. T. S. Piper and G. Wilkinson, *Chem. Ind. (London)*, p. 1296 (1955).
70. T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.* **1**, 165 (1955).
71. T. S. Piper and J. Wilkinson, *J. Inorg. Nucl. Chem.* **2**, 38 (1956).
72. T. J. Curphey, J. O. Senter, M. Rosenblum, and J. H. Richards, *J. Am. Chem. Soc.* **82**, 5249 (1960).
- 72a. A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.* p. 1133 (1963).
73. H. Nöth and R. Hartwimmer, *Chem. Ber.* **93**, 2238 (1960).
74. M. Rosenblum, Ph.D. thesis, Harvard Univ., Cambridge, Massachusetts, 1953; as cited in ref. (75).
75. M. Rosenblum, *Chem. Ind. (London)*, **30**, 953 (1958).
76. A. N. Nesmeyanov, L. A. Kazitsyna, B. U. Lokshin, and I. I. Kritskaya, *Dokl. Akad. Nauk SSSR* **117**, 433 (1957).
77. K. L. Rinehart, Jr., K. L. Motz, and S. Moon, *J. Am. Chem. Soc.* **79**, 2749 (1957).
78. A. N. Nesmeyanov and L. A. Kazitsyna, *Dokl. Akad. Nauk SSSR* **125**, 1037 (1959).
79. M. Rosenblum, *J. Am. Chem. Soc.* **81**, 4530 (1959).
80. P. L. Pauson, *J. Am. Chem. Soc.* **76**, 2187 (1954).
81. M. Rosenblum and W. G. Howells, *J. Am. Chem. Soc.* **84**, 1167 (1962).
82. K. L. Rinehart, Jr. and R. J. Curby, Jr., *J. Am. Chem. Soc.* **79**, 3290 (1957).
83. K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *J. Am. Chem. Soc.* **79**, 3420 (1957).
84. H. E. Rubalcava and J. B. Thomson, *Spectrochim. Acta* **18**, 449 (1962).
85. K. Schlögl and H. Seiler, *Tetrahedron Letters* **7**, 4 (1960).
86. K. Schlögl and M. Peterlik, *Tetrahedron Letters* **13**, 573 (1962).
87. K. Schlögl, M. Peterlik, and H. Seiler, *Monatsh. Chem.* **93**, 1309 (1962).
88. K. Schlögl and M. Peterlik, *Monatsh. Chem.* **93**, 1328 (1962).
89. M. D. Rausch, E. O. Fischer, and H. Grubert, *Chem. Ind. (London)* **30**, 756 (1958).
90. M. D. Rausch, E. O. Fischer, and H. Grubert, *J. Am. Chem. Soc.* **82**, 76 (1960).

91. E. O. Fischer and K. Plesske, *Chem. Ber.* **91**, 2719 (1958).
92. F. A. Cotton and J. R. Leto, *Chem. Ind. (London)* **30**, 1368 (1958).
93. R. Riemschneider and H. G. Kassahn, *Z. Naturforsch.* **14b**, 348 (1959).
94. J. Kozikowski, R. L. Maginn, and M. S. Klove, *J. Am. Chem. Soc.* **81**, 2995 (1959).
95. F. Calderazzo, R. Rebaudo, and R. Ercoli, *Chim. Ind. (Milan)* **42**, 52 (1960).
96. E. O. Fischer and K. Plesske, *Chem. Ber.* **93**, 1006 (1960).
97. R. Riemschneider, O. Goehring, and M. Krieger, *Monatsh. Chem.* **91**, 307 (1960).
98. E. O. Fischer and K. Plesske, *Chem. Ber.* **94**, 93 (1961).
99. E. W. Neuse and D. S. Trifan, *J. Am. Chem. Soc.* **84**, 1850 (1962).
100. G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.* **2**, 32 (1956).
101. R. Schneider, Ph.D. thesis, Univ. Munich, Munich, Germany, 1962.
102. G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, p. 362. Van Nostrand, Princeton, New Jersey, 1945.
103. F. A. Miller and B. L. Crawford, Jr., *J. Chem. Phys.* **14**, 282 (1946); **17**, 249 (1949).
104. M. A. Kovner, *Zh. Eksperim. i. Teor. Fiz.* **26**, 598 (1954).
105. D. H. Whiffen, *Phil. Trans. Roy. Soc. (London)* **A248**, 131 (1955).
106. C. R. Bailey, C. K. Ingold, H. G. Poole, and C. L. Wilson, *J. Chem. Soc.* p. 912 (1936); p. 222 (1946).
107. A. Langseth and R. C. Lord, *Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd.* **16** (6) (1938).
108. R. S. Halford and O. A. Shaefer, *J. Chem. Phys.* **14**, 141 (1946).
109. R. D. Mair and D. F. Hornig, *J. Chem. Phys.* **17**, 1236 (1949).
110. F. A. Miller, *J. Chem. Phys.* **24**, 996 (1956).
111. S. Brodersen and A. Langseth, *Kgl. Danske Videnskab. Selskab Mat. Fys. Skrifter.* **1** (1) (1956).
112. E. Ruch, *Chem. Ges. DDR, Hauptjahrestagung 1955, Proc.* p. 125. Akademie Verlag, Berlin, 1956.
113. H. P. Fritz and W. Lüttke, *5th Intern. Conf. Coord. Chem. London (1959) J. Chem. Soc. Spec. Publ.* **13**, 123 (1959).
114. F. Jelinek, *Nature* **187**, 871 (1960).
115. R. G. Snyder, *Spectrochim. Acta* **15**, 807 (1959).
116. E. Weiss and E. O. Fischer, *Z. Anorg. Allgem. Chem.* **286**, 142 (1956).
- 116a. F. A. Cotton, W. A. Dollase, and J. S. Wood, *J. Am. Chem. Soc.* **85**, 1543 (1963).
117. E. O. Fischer, H. P. Fritz, J. Manchot, E. Priebe, and R. Schneider, *Chem. Ber.* **96**, 1418 (1963).
118. H. P. Fritz and J. Manchot, *Z. Naturforsch.* **17b**, 711 (1962).
- 118a. G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 3807 (1961).
119. M. S. Ashkanazi, P. U. Kurnosova, and V. S. Finkelstein, *Zh. Fiz. Khim.* **8**, 438 (1936).
120. Sh. Sh. Raskin, *Dokl. Akad. Nauk SSSR* **100**, 485 (1955).
121. Sh. Sh. Raskin, *Opt. i Spektroskopiya* **1**, 516 (1956).
122. L. W. Daasch, *Spectrochim. Acta* **9**, 726 (1959).
123. J. Manchot, Ph.D. thesis, Tech. Hochschule, Munich, Germany, 1963.
- 123a. R. E. Rundle and J. H. Goring, *J. Am. Chem. Soc.* **72**, 5337 (1950).
- 123b. Sh. Sh. Raskin, *Dokl. Akad. Nauk SSSR* **141**, 900 (1961).
124. H. P. Fritz and J. Manchot, *Chem. Ber.* **96**, 1891 (1963).
125. R. S. Drago, J. T. Kwon, and R. D. Archer, *J. Am. Chem. Soc.* **80**, 2667 (1958).
126. E. O. Fischer, unpublished results.
127. G. D. Walker, personal communication to E. O. Fischer.
128. E. O. Fischer and H. Brunner, *Z. Naturforsch.* **16b**, 406 (1961).

129. T. F. Burger and H. H. Zeiss, *Chem. Ind. (London)* p. 183 (1962).
130. H. Brunner, personal communication.
131. J. P. Mortensen, Ph.D. thesis, Tech. Hochschule, Munich, Germany, 1960.
132. R. E. Humphrey, *Spectrochim. Acta* **17**, 93 (1961).
133. R. D. Nelson, W. G. Fateley, and E. R. Lippincott, *J. Am. Chem. Soc.* **78**, 4870 (1956).
134. W. G. Fateley, B. Curnutte, and E. R. Lippincott, *J. Chem. Phys.* **26**, 1471 (1957).
135. E. O. Fischer and H. P. Fritz, *Z. Physik. Chem. (Frankfurt)* [N.S.] **17**, 132 (1958).
136. H. J. Dauben and L. R. Honnen, *J. Am. Chem. Soc.* **80**, 5570 (1958).
137. R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.* **81**, 5263 (1959).
138. R. P. M. Werner and S. A. Manastyrskyj, *J. Am. Chem. Soc.* **83**, 2023 (1961).
139. J. D. Munro and P. L. Pauson, *J. Chem. Soc.* pp. 3475, 3479 (1961).
140. M. S. C. Flett, W. T. Cave, E. E. Vago, and H. W. Thompson, *Nature* **159**, 739 (1947).
141. E. R. Lippincott, R. C. Lord, and R. S. McDonald, *J. Am. Chem. Soc.* **73**, 3370 (1951).
142. O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).
143. H. P. Fritz and H. Keller, *Z. Naturforsch.* **16b**, 231 (1961).
144. H. P. Fritz and H. Keller, *Chem. Ber.* **95**, 158 (1962).
- 144a. F. S. Mathews and W. N. Lipscomb, *J. Am. Chem. Soc.* **80**, 4745 (1958).
145. B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.* **83**, 4862 (1961).
146. B. Dickens and W. N. Lipscomb, *J. Chem. Phys.* **37**, 2084 (1962).
147. H. P. Fritz and H. Keller, *Chem. Ber.* **95**, 820 (1962).
148. T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.* **82**, 366 (1960).
149. F. A. Cotton, *J. Chem. Soc.* p. 400 (1960).
150. B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.* **83**, 489 (1961).
151. H. P. Fritz, in "Advances in the Chemistry of the Coordination Compounds" (S. Kirschner, ed.), Proc. 6th Intern. Conf. Coord. Chem., Detroit, 1961. Macmillan, New York.
152. J. R. Doyle, J. H. Hutchinson, N. C. Baenziger, and L. W. Tresselt, *J. Am. Chem. Soc.* **83**, 2768 (1961).
153. A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan* **33**, 425 (1960).
154. H. P. Fritz and H. Keller, *Z. Naturforsch.* **16b**, 348 (1961).
155. A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 4821 (1962).
156. K. S. Brenner, E. O. Fischer, H. P. Fritz, and C. G. Kreiter, *Chem. Ber.* **96**, 2632 (1963).
157. G. J. Bethlenfalvay, Diplom. thesis, Univ. Munich, Munich, Germany, 1962.
158. E. R. Lippincott and R. D. Nelson, *J. Am. Chem. Soc.* **77**, 4990 (1955).

SUPPLEMENTARY REFERENCES

1. F. A. Cotton *et al.*, *J. Inorg. Nucl. Chem.* **1**, 175 (1955) [Cyclopentadienylmetal carbonyls]
2. E. O. Fischer and U. Zahn, *Chem. Ber.* **92**, 1624 (1959) [$Cp(Ir,Rh)C_5H_6$].
3. E. O. Fischer, N. Kriebitzsch, and R. D. Fischer, *Chem. Ber.* **92**, 3214 (1959) [aromatic- $Cr(CO)_3$]
4. E. O. Fischer and A. Löchner, *Z. Naturforsch.* **15b**, 266 (1960) [$TiCp_3$]
5. E. O. Fischer, K. Ulm, and H. P. Fritz, *Chem. Ber.* **93**, 2167 (1960) [$(CpCrO)_4$]
6. E. O. Fischer, H. P. Kögler, and P. Kuzel, *Chem. Ber.* **93**, 3006 (1960) [$CpMnC_4H_6(CO)$]

7. E. O. Fischer and K. Bittler, *Z. Naturforsch.* **16b**, 225 (1961) [$\text{CpRh}(\text{CO})_2$]
8. E. O. Fischer and G. E. Herberich, *Chem. Ber.* **94**, 1517 (1961) [$\text{CpCoC}_5\text{H}_5\text{—R}$]
9. E. O. Fischer and K. Ulm, *Chem. Ber.* **94**, 2413 (1961) [$\text{CpCrC}_5\text{H}_7(\text{CO})_2$]
10. H. P. Fritz, *Chem. Ber.* **94**, 1217 (1961) [CpNiC_5H_7]
11. H. P. Fritz and H. J. Keller, *Chem. Ber.* **95**, 2259 (1962) [$\text{Co}_2\text{C}_{25}\text{H}_{24}$]
12. M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 3753 (1959) [$\text{Cp}(\text{Co,Rh})\text{C}_5\text{H}_6$]
13. M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* p. 989 (1960) [CpFeC_6H_7]
14. B. F. Hallam and P. L. Pauson, *Chem. Ind. (London)* p. 653 (1955) [$\text{CpFe}(\text{CO})_2\text{C}_5\text{H}_5$]
15. B. F. Hallam and P. L. Pauson, *J. Chem. Soc.* p. 3030 (1956) [$(\text{CpFe}(\text{CO})_2)_2$]
16. R. B. King, P. M. Treichel, and F. G. A. Stone, *Chem. Ind. (London)* p. 747 (1961) [$\text{CpFe}(\text{CO})_2\text{—M}(\text{CO})_x$]
17. J. G. Murray, *J. Am. Chem. Soc.* **83**, 1287 (1961) [$\text{Cp}_2\text{Ti}(\text{CO})_2$]
18. T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.* **3**, 104 (1956) [$\text{CpM}(\text{CO})_x\text{—R}$, $\text{CpM}(\text{NO})_2\text{—R}$]
19. R. L. Pruett and E. L. Morehouse, *Chem. Ind. (London)* p. 980 (1958) [$\text{CpRe}(\text{CO})_3$]
20. G. Wilkinson, *J. Am. Chem. Soc.* **76**, 209 (1954) [$[\text{CpMo}(\text{CO})_5\text{MoCp}]$]
21. S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Japan* **30**, 647 (1957) [$\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$]
22. H. H. Zeiss and W. Herwig, *Ann. Chem.* **606**, 209 (1957) [$\text{Cr}(\text{C}_6\text{H}_5\text{D})_2$]

AUTHOR INDEX

Numbers in parentheses are reference numbers and indicate that an author's work is referred to although his name is not cited in the text. Numbers in *italics* show the page on which the complete reference is listed.

A

Abel, E. W., 18(52), 19(52), 21(52), 25(52), 26(52), *44*
 Adkins, H., 116(97), *140*
 Aldrich, P. E., 203(148a), *220*
 Alimarin, I. P., 48(8), *85*
 Allen, C. F. H., 224, 225, *238*
 Alleston, D. L., 72(74), 73(74), *87*
 Amberger, E., 49(25), *86*
 Anderson, R. P., 104(48), 113(48), *139*
 Anisimov, K. N., 29(87), *45*
 Anthes, J. A., 226, *238*
 Archer, R. D., 300(125), *314*
 Arest-Yakubovich, P. E., 48(8), *85*
 Armour, A. G., 50(35), 51(35), *86*
 Armstrong, M. D., 229(29), *238*
 Arnet, J. E., 15(43), 16(43), 28(43), *44*
 Ashkanazi, M. S., 300(119), *314*
 Asinger, F., 17, *44*
 Atwell, W. H., 116(92), 117(92), 119(92), 120(101), 122(101), 135(92, 101), *140*
 Avram, M., 261(54, 55), *313*

B

Baenziger, N. C., 307(152), *315*
 Bailey, C. R., 291(106), 295(106), *314*
 Baker, E. D., 154(48), *217*
 Balint, A. E., 151(25), *217*
 Banks, R. E., 144, 145(5), 161(5), 162(5), 201(5), 202(5), *216*
 Barrow, G. M., 243(26), 244(26), 246(26), *312*
 Barry, A. J., 53(43), *86*
 Bartocha, B., 155(49), 160(59), *217*
 Bastiansen, O., 304(142), 306(142), *315*
 Baum, G. A., 108(78), *140*
 Bayer, A., 231, *238*
 Beck, W., 179(96, 100), 185(100), 187(96), 188(100), 189(96, 100), *218*
 Becker, E. I., 51(38), 59(38), 70(33), 74(76), 75(77), 78(77), 84(81), *86, 87*

Beel, J. A., 146(8), *216*
 Beg, M. A. A., 167(76), 168(76), *218*
 Bell, A., 225, *238*
 Bellamy, L. J., 241, 243(20), *312*
 Bennet, O. F., 108(81), 109(81), 126(81), *140*
 Berg, O., 17, *44*
 Bergman, E., 200(145), 201(145), *220*
 Bergmann, E., 234(50, 51), *238*
 Bertelli, D. J., 10(27), 14(27), 21(27), 30, 31(27), *43*
 Berthold, A. J., 184(121a), *219*
 Bethlenfalvay, G. J., 307(157), 308(157), *315*
 Beumel, O. F., Jr., 61(60), 66(63, 64), 68(67), 69(63), *86, 87*
 Bier, G., 164(71), *218*
 Bilbo, A. J., 160(59), *217*
 Birchall, J. M., 156(51), *217*
 Bird, C. W., 18(56, 58), 19(56, 58), *44*
 Birmingham, J. M., 254(41), 279(64a), *312, 313*
 Bittler, K., *316*
 Blank, H., 223(8), *237*
 Blum-Bergmann, O., 234(50), *238*
 Bode, G., 233(49), 234(49), *238*
 Böhler, F., 164(69), *218*
 Boekelheide, V., 227(24), *238*
 Bond, A. C., Jr., 48(9), 51(9), *85*
 Bor, G., 250(32), *312*
 Borer, K., 90(3), 91(3), *137*
 Boston, J. L., 28(86), 40(86), *45, 196(135, 136), 198(136), 199(136), 208(136), 219*
 Bourn, A. J., 206(153a), *220*
 Brändle, K., 153(38, 39), 167(39), 172(39), 213(39), *217*
 Brandmüller, J., 246(28), 252(28), *312*
 Brandon, M., Sister, 109(83), *140*
 Braye, E. H., 3(8), 15(38), 26(38), 27(78, 79), 39(8), 40(8, 38), 41(38, 128, 131), *43, 44, 45, 46*

- Breslow, D. S., 182(115), 190(115, 127), 193(127, 129), 219
 Breslow, R., 257(45), 312
 Breuner, K. S., 307(156), 315
 Brinckman, F. E., 171(80), 172(80), 218
 Brindell, G. D., 77(78), 87
 Brodersen, S., 292(111), 295(111), 314
 Brook, A. G., 106(57), 139
 Brown, D. A., 3(8), 5(16), 6(16), 7(24), 23(16), 27(80), 39(8), 38(120), 40(8, 16), 41(16, 24, 80, 119, 130), 43, 45, 46
 Brown, H. C., 109(83), 140
 Brügel, W., 243(27), 249(27), 251(27), 252(27), 312
 Brunner, H., 301(128, 130), 315
 Buckingham, A. D., 206(153), 207(153), 220
 Buisson, R., 85(84), 87
 Burg, A. B., 51(40), 86, 153(44), 154(48), 171(81), 178(90), 217, 218
 Burger, T. F., 301(129), 315
 Burkhard, C. A., 53(42), 86, 92(16), 104(16, 47), 106(16), 113(16), 136(16), 138, 139
 Burns, J. H., 91(10), 138
 Burton, R., 14(40), 18(52), 19(52), 21(40, 52), 22(40), 25(52, 73), 26(52, 73), 31(40), 44
- C**
- Cais, M., 15(35), 44
 Calas, R., 49(20b), 66(65), 69(71), 70, 85, 87
 Calderaro, E., 223, 237
 Calderazzo, F., 180(104), 219, 286(95), 314
 Campbell, K. N., 222, 237
 Campbell, P. G., 108(81), 109(81), 126(81), 140
 Caplier, I., 27(79), 45
 Cartledge, F. K., 125(103), 140
 Case, J. R., 38, 45, 46
 Cave, W. T., 304(140), 315
 Chainani, G. R., 100(38), 106(38), 107(38), 127(38, 104), 134(38, 104), 135(38, 104), 139, 141
 Chambers, R. D., 157(57), 158(57), 159(57a), 166(74), 169(74), 171(57), 172(57a), 204(151), 205(151), 207(152, 154), 217, 218, 220
 Chambers, R. F., 49(24), 86
 Chang, H. W., 257(45), 312
 Chang, K. Y., 114(89), 122(102), 126(104), 127(102), 134(102), 135(102, 104), 140, 141
 Chapman, D. R., 116(94, 95), 119(94, 95), 120(94, 95), 125(94), 128(95), 140
 Charrier, G., 224, 238
 Chatt, J., 176, 181(108), 182(116), 190(116), 193(87, 88), 218, 219, 240(11), 257(11), 311
 Chaudet, J. H., 99(35), 110(35), 117(35), 135(35), 138
 Chaudhari, M. A., 150(19c), 185(123a), 187(123a), 188(123a), 191(123a), 216, 219
 Chivers, T., 159(57a), 172(57a), 217
 Churchill, M. R., 199(142a), 208(142a), 220
 Clar, E., 224, 238
 Clark, H. C., 144, 145(5a), 146(8), 147(9), 157(57), 158(57), 161(9), 165(72), 166(72, 74, 75), 167(9, 75, 76, 78a), 168(9, 76, 78a), 169, 171(57, 75), 207(152, 154), 216, 217, 218, 220
 Clarkson, R., 3(10), 37(10), 38(10, 121), 43, 46
 Clauss, A., 3(8), 39(8), 40(8), 43
 Cleveland, F. F., 241(18), 311
 Closson, R. D., 178(93, 94), 180(94), 193(93, 94), 218
 Coates, G. E., 91(6a), 99(6a), 137, 184(121), 204(151), 205(151), 219, 220
 Coe, P. L., 149(19), 150(19), 216
 Coffey, C. E., 35(106), 45, 240(9), 257(9), 311
 Coffield, T. H., 178(93, 94), 180(94), 193(93, 94), 218
 Colinese, D. L., 18(58), 19(58), 44
 Connor, R., 116(97), 117(92), 140
 Considine, W. J., 48(17), 85
 Cookson, R. C., 18(56, 58), 19(56, 58), 44
 Cooper, S., 100(38), 106(38), 107(38), 114(87, 88), 116(88), 126(87, 88, 104), 127(38), 134(38, 104), 135(38, 87), 136(87), 139, 140
 Cotton, F. A., 3(9), 5(17), 6(17), 23(17, 69), 39(9, 125), 43, 44, 46, 180(104), 219, 240(6), 241(22), 250(33), 252(22, 39), 254(41), 255, 277(39), 279(39), 281(66), 284(70), 286(92), 298(116a), 307(149), 311, 312, 313, 314, 315

Coulson, C. A., 91(8), 138, 258(48), 312
 Coyle, T. D., 156(52, 53), 157(53, 56), 165
 (56), 181(110), 188(110), 207(56), 208
 (110), 209(110), 212(56), 217, 219
 Crawford, B. L., Jr., 255, 291(103), 312,
 314
 Cristol, S. J., 77(78), 87
 Cross, P. C., 247(29), 291(29), 292(29),
 297(29), 299(29), 312
 Cserr, R., 151(25), 217
 Curby, R. J., Jr., 286(82, 83), 313
 Curnutte, B., 254(40), 266(40), 268(40),
 302(134), 303(134), 312, 315
 Curphey, T. J., 284(72), 286(72), 313

D

Daasch, L. W., 300(122), 314
 Dabrowska, D., 133(107), 141
 Dahl, L. F., 7, 9(23), 41, 43, 46, 196(135),
 198(133), 199(133), 219
 Dauben, H. J., 10(27), 14(27), 21(27), 30,
 31(27), 43, 45, 303(136), 315
 Davison, A., 10(28), 12(30, 31), 23(28),
 24(28), 31(28, 30, 31, 92), 43, 45, 281
 (67), 307(155), 313, 315
 Decius, J. C., 247(29), 291(29), 292(29),
 297(29), 299(29), 312
 Dent, W. T., 198(140a), 220
 Dergunov, Y. I., 99(36), 139
 De Pree, L., 53(43), 86
 Dewar, M. J. S., 9, 43
 Dickens, B., 5, 9(14), 13(14), 23(13, 14,
 15), 43, 306(145, 146), 307(146, 150),
 315
 Dillard, C. R., 48(11, 15), 51(11, 15), 85
 Dixon, S., 148(18), 164(18), 216
 Doak, G. O., 176, 178, 218
 Dodge, R. P., 40(127), 46, 258(49), 312
 Dollase, W. A., 298(116a), 314
 Donadio, R. E., 153(42), 161(42), 217
 Doyle, J. R., 307(152), 315
 Drago, R. S., 300(125), 314
 Dubeck, M., 198(141), 220
 Duffaut, N., 66(65), 87
 Dufraisie, C., 225, 238
 Duncanson, L. A., 198(140a), 220
 Dunitz, J. D., 240(14), 258(50), 311, 312
 Dunn, G. E., 98(33), 106(33), 107(70),
 129(70), 138, 140

E

Eaborn, C., 90(1), 91(8), 107(1), 108(1),
 113(1), 133(1), 134(1), 137, 138
 Eichler, S., 20(61), 23, 44
 Eidt, S. H., 106(52), 134(52), 139
 Eiland, P. F., 240(12), 311
 Eisch, J., 53(45), 86
 Eliel, E. J., 68(68), 87
 El-Sayed, M. A., 214(156), 220
 Emel  us, H. J., 48(12), 51(12), 85, 144,
 145(1, 2, 6), 150(6), 178(1, 2), 200(6),
 201(1, 2), 203(149), 204(150), 216,
 220
 Emerson, G. F., 14(42), 16(42), 17(50), 18
 (42), 19(42), 34(42, 50), 36(42), 44
 Emilius, M., Sister, 48(6), 85
 Emmons, W. D., 235(57), 238
 Engelhardt, V. A., 60(57), 86, 167(78),
 168(78), 218
 Ercoli, R., 286(95), 314
 Evans, F. W., 79(80), 87
 Eyring, H., 243(23), 244(23), 246(23), 312

F

Fainberg, A. H., 200(145), 201(145), 220
 Fang, F. T., 237(59), 238
 Farlow, M. W., 233(45), 238
 Fateley, W. G., 302(133, 134), 303(134),
 315
 Feldkimmel, M., 15(35), 44
 Fichtel, K., 31, 32, 33, 45
 Filbey, A. H., 180(103), 219
 Finholt, A. F., 48(9), 51(9), 85
 Finkelstein, V. S., 300(119), 314
 Fischer, A. K., 53(44), 86
 Fischer, E. O., 21, 30, 31, 32, 33, 44, 45,
 240(5, 8, 13), 274, 277(63), 284(63),
 286(89, 90, 91, 96, 98), 292(8), 293
 (116), 298(117), 301(8, 126, 128), 303
 (135), 307(156), 311, 312, 313, 314,
 315
 Fischer, R. D., 30, 45, 281(68), 313, 315
 Fletcher, R. S., 109(83), 140
 Flett, M. S. C., 304(140), 315
 Folkers, A., 116(97), 140
 Forneris, R., 252(38), 257(38), 268(38),
 274(38), 293(38), 295(38), 296(38),
 312

Fox, R. J., 79(80), 87
 Francis, W. C., 151, 216
 Frank, R. L., 233(46), 238
 Freeman, J. P., 231(38), 238
 Freund, M., 233(48, 49), 234(49), 238
 Friedel, R. A., 37(116, 117), 38(116, 117), 45, 197(137), 219
 Fritz, H., 164(71), 218
 Fritz, H. P., 21(63), 23(67, 68), 44, 240(5, 8, 10), 251(36), 252(38), 257(10, 38, 44), 258(10), 259(51), 260(36, 52), 261(36, 52, 53, 54, 55), 266(57), 268(38, 57), 274(38, 59), 277(57, 63), 284(10, 63), 292(8), 293(38, 44, 113), 295(38), 296(38), 298(117), 299(44, 118), 300(124), 301(8), 303(135), 305(143, 144), 306(144), 307(144, 147, 151, 154, 156), 310(36), 311, 312, 313, 314, 315, 316
 Fuchs, R., 53(46), 86
 Fulton, R. F., 65, 87
 Furnival, S., 167(78a), 168(78a), 218
 Furth, K., 47, 48(1), 85
 Fuson, R. C., 222(3), 227(25), 228(27, 28), 229(29, 30), 230(31, 32, 35), 231(36, 37), 232(42, 44), 233(45, 47), 234(55), 235(56, 57), 237(59), 237, 238

G

Gaertner, R., 230(31), 254(53), 238
 Gainer, G. C., 234(52), 238
 Gaj, B. J., 106(63), 117(99), 125(99), 139, 140
 Galli, A., 232(42), 238
 Gerloch, M., 199(142a), 208(142a), 220
 Geyer, A. M., 161(62), 218
 Gibson, D. H., 10(25), 34(25), 43
 Gilkey, J. W., 53(43), 86
 Gillies, D., 206(153a), 220
 Glover, C. A., 101(42, 43), 139
 Goldman, M., 227(24), 238
 Goldschmidt, S., 234(54), 238
 Geissman, T. A., 227, 238
 Ghigi, E., 224, 238
 Gilman, H., 53(45, 46), 86, 92(17, 18, 19), 94(26), 97(29), 98(33), 99(18, 35), 100(18, 38, 39), 101(41, 43, 44), 102(41, 45), 103(41), 104(41), 105(41, 49, 49a),

106(26, 33, 38, 39, 49a, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64), 107(17, 38, 39, 54, 55, 67, 70, 71), 110(17, 18, 19, 34, 35), 111(84), 112(84, 85), 113(26, 34, 41, 49, 86), 114(41, 49a, 85, 87, 88, 89, 90), 115(17, 18, 41, 49a, 90a, 91), 116(17, 18, 41, 49a, 84, 88, 92, 93, 94, 95, 96), 117(17, 35, 85, 99, 100), 118(34, 91, 96), 119(17, 92, 94, 95), 120(93, 94, 95, 101), 121(84, 90), 122(90, 102), 123(29, 96), 124(49a), 125(17, 18, 41, 49a, 94, 99, 103), 126(41, 49a, 87, 90, 100, 104), 127(18, 29, 38, 41), 128(95), 129(18, 70, 90, 95, 102), 130(41, 91a), 131(41), 132(41, 105), 133(49), 134(18, 26, 38, 41, 49, 52, 55, 67, 86, 90a, 102, 104), 135(17, 18, 19, 29, 34, 35, 38, 41, 49a, 87, 92, 95, 101, 102, 104), 136(34, 41, 49a, 87, 90a, 100), 137(17), 138, 139, 140, 141, 171(82), 218, 222, 223, 225, 234(52), 237, 238
 Gist, W. J., 232, 238
 Glaze, W., 277(61), 313
 Goehring, O., 286(97), 314
 Goldwhite, H., 203(148), 220
 Goodman, J. J., 106(52), 107(67), 134(52, 67), 139
 Goring, J. H., 300(123a), 314
 Goubeau, J., 154, 217
 Graham, W. A. G., 155(49), 217
 Green, C., 10(26), 43
 Green, M., 19, 44
 Green, M. L. H., 5, 10(28), 12, 15(12), 18(52, 54), 19(52, 54), 21(52), 23(28), 24(28), 25(52), 26(52), 31(28), 33, 35, 41(54), 42(54), 43, 44, 45, 181(114), 219, 280(65), 281(67), 284(65), 285(65), 313, 316
 Greenfield, H., 197(137), 219
 Greer, W. N., 49(23), 86
 Grieshaber, E. W., 234(55), 238
 Griffin, G. W., 228(27), 238
 Griffiths, J. E., 178(90), 218
 Groh, G., 184(121a), 219
 Grubert, H., 286(89, 90), 313
 Gruhl, A., 2(1), 15(1), 18(1), 43
 Guter, G. A., 106(52), 139
 Guy, R. G., 196(132), 198(140a), 200(132), 219, 220, 240(11), 257(11), 311

H

- Hagihara, N., 6(20), 16(44), 18(44), 22(20, 44), 23(20), 43, 44, 307(153), 315
 Haken, W., 48(3), 85
 Halford, R. S., 291(108), 314
 Hallam, B. F., 2, 14(4), 15(4), 23(70), 25(72), 43, 44, 316
 Hammond, G. S., 49(20d), 70(20d), 86
 Harrah, L. A., 104(46), 139
 Harrell, R., 114(88), 116(88), 117(100), 126(88, 100), 136(100), 140
 Hart, F. A., 181(108), 219
 Hartwinner, R., 284(73), 285(73), 313
 Hartzfeld, H. A., 106(52), 139
 Harzdorf, C., 106(66), 129(66), 139
 Haszeldine, R. N., 144, 145(3, 4, 5, 6), 146(3), 150(6, 20), 151(23, 26), 156(51), 161(4, 5, 61, 62), 162(5, 66), 163(66, 67), 191(67), 200(6, 144), 201(3, 4, 5, 146), 202(5), 203(148, 149), 216, 217, 218, 220
 Hauptschein, M., 159(58), 160(58), 217
 Heck, R. F., 182(115), 190(115, 127), 193(127, 129), 219
 Hedberg, K., 304(142), 306(142), 315
 Hedberg, L., 304(142), 306(142), 315
 Heinrich, F., 91(11), 138
 Hellmann, M., 153(41), 161(41), 217
 Hellman, R. J., 230(31), 238
 Hengge, E., 92(19a), 104(47), 138, 139
 Henne, A. L., 151, 216
 Henry, M. C., 53(50), 55(50), 61, 86
 Herber, R. H., 7(22), 43
 Herberich, G. E., 316
 Herwig, W., 316
 Herzberg, G., 243(24), 244(24), 246(24), 247(24), 248, 249(24, 30), 250(31), 291(102), 308(24), 312, 314
 Heymann, E., 49(20a), 70(20a), 85
 Hieber, W., 179(96, 100, 101), 185(100), 187(96), 188(100, 101), 189(96, 100, 101), 193(101), 218, 219
 Hock, A. A., 3(6), 38, 43, 45
 Hoehn, H. H., 28(85), 45, 181(112), 188(112), 195(112), 196(112), 199(112), 200(112), 208(112), 216(112), 219
 Hoffman, A., 233(45), 238
 Holmes, J. D., 31(93), 45
 Holmes, J. M., 167(77a), 172(77a), 218
 Honnen, L. R., 30(88), 45, 303(136), 315

- Hoogzand, C., 3(8), 39(8), 40(8), 41(128), 43, 46
 Hook, D. E., 53(43), 86
 Horclois, R., 225, 238
 Hornig, D. F., 291(109), 314
 Howard, E. G., 203(148a), 207(148a), 220
 Howells, W. G., 286(81), 313
 Huber, M. L., 223, 227(26), 237, 238
 Hudec, J., 18(56, 58), 19(56, 58), 44
 Hübel, W., 3(8), 15(38), 26(38, 75), 27(77, 78, 79), 36, 39, 40(8, 38, 126), 41(38, 77, 78, 128, 131, 132), 42, 43, 44, 45, 46, 199(142), 220
 Hüchel, W., 107(76), 140
 Huggins, D. K., 279(64), 280(64), 313
 Humphrey, R. E., 302(132), 315
 Hutchinson, J. H., 307(152), 315

I

- Irhman, K. G., 34, 45
 Impastato, F. J., 34, 45
 Ingham, R. K., 106(54), 107(54), 139, 171(82), 218
 Ingold, C. K., 291(106), 295(106), 314
 Ishikawa, M., 107(72), 140

J

- Jackson, H. L., 222(3), 234(55), 237, 238
 Jaffe, H. H., 176, 178, 218
 Jakusik, E. R., 168(77), 169(77), 218
 Jarvie, A. W. P., 92(17, 18), 97(29), 99(18, 35), 100(39), 106(39), 107(17, 39), 110(17, 18, 35), 114(90), 115(17, 18), 116(17, 18, 93), 117(17, 35), 119(17), 120(93), 121(90), 122(90), 123(29), 125(17, 18), 126(90, 90a, 91), 127(18, 29), 129(18, 90), 134(18), 135(17, 18, 29, 35), 138, 139, 140
 Jellinek, F., 293(114), 298(114), 314
 Johannesen, R. B., 109(83), 140
 Johannsen, A., 48(4), 85
 Johncock, P., 148(17), 216
 Jolly, P. W., 180(102), 189(102), 219
 Jolly, W. L., 50(30, 31), 51(31), 86
 Jones, E. R. H., 3(10), 37(10), 38(10, 120, 121, 123), 43, 45, 46
 Jones, R. G., 223(8), 237

Jones, R. N., 251(35), 312
 Judd, G. F., 146(7), 216
 Julian, P. L., 232, 238
 Jun, Mon-Jon, 36(112), 45
 Juvinall, G. L., 154(48), 217

K

- Kaesz, H. D., 26(74), 27(74), 44, 148(10, 14), 152(14), 153(14, 37, 46), 166(46, 73), 167(37, 46), 169(46, 73), 170(37, 46), 171(46), 172(37), 174(46), 178(91), 179(91), 180(91), 183(91), 187(91), 188(91), 189(91), 192(10), 213(37), 214(46, 156), 216, 217, 218, 220, 279(64), 280(64), 313
 Kaiser, E. W., 242(44), 238
 Kaplan, L., 241(15), 311
 Kassahn, H. G., 286(93), 314
 Katz, J. J., 241(15), 311
 Kazitsyna, L. A., 286(76, 78), 313
 Kealy, T. J., 240(3), 311
 Keblys, K. A., 180(103), 219
 Keller, H., 23(67), 44, 240(10), 257(10), 258(10), 261(54, 55), 284(10), 305(143, 144), 306(144), 307(144, 147, 154), 311, 313 315, 316
 Kemmitt, R. D. W., 183(118), 188(118), 191(118), 219
 Kennedy, W. D., 99(35), 110(35), 117(35), 135(35), 138
 Kester, W. L., 241(15), 311
 Kettle, S. F. A., 35(107), 45, 48(12), 51(12, 36), 85, 86
 Kharasch, M. S., 230, 238
 Kiesel, R. J., 74(75), 87
 Kimball, G. E., 243(23), 244(23), 246(23), 312
 King, G. D. S., 3(8), 15(34), 16(34), 18(34), 19(60, 62), 22(34, 65), 25(65), 26(74, 76), 27(74, 76, 84), 28(34), 29(34), 32(95), 39(8), 40(8), 41, 43, 44, 45, 46
 King, R. B., 178(91), 179(91, 97a, 98, 99), 180(91, 99, 102b, 105), 181(98, 110), 183(91), 184(99), 187(91, 92, 97a, 98, 99), 188(91, 98, 99, 105, 110), 189(91, 97a, 102b), 190(99), 191(99), 208(110), 209(110), 218, 219, 303(137), 315, 316
 Kinney, C. R., 222(4), 237
 Kipping, F. S., 92(13, 14, 15), 94, 95, 96, 97, 98, 99, 101, 102, 103, 104, 106(25), 107(69), 108(28), 110, 113, 116(13, 28), 117(98), 119, 120, 123, 124(28), 127, 129, 130(14), 135(13, 15, 27), 137, 138, 139, 140
 Kirby, J. E., 222(4), 237
 Kirby, R. H., 223(7), 237
 Klein, R. A., 106(61), 139
 Klove, M. S., 286(94), 314
 Knoth, W. H., Jr., 108(80), 140
 Knunyants, I. L., 148(13), 152(13, 30, 32, 33, 34, 35), 153(34, 35, 36), 163(33), 216, 217
 Kochar, R., 14(41), 17(41), 44
 Kögler, H. P., 315
 Koelsch, C. F., 223, 224(12, 13), 226, 238
 Koerner von Gustorf, E., 36(112), 45
 Kohler, E. P., 221, 237
 Kohlrausch, K. W. F., 243(25), 244(25), 246(25), 248, 308(25), 312
 Kolonova, N. E., 29(87), 45
 König, K., 50(33), 86
 Koreshtshkov, Y. D., 258(47), 312
 Kosheshkov, K. A., 277(60), 313
 Kovner, M. A., 291(104), 314
 Kozikowski, J., 178(93, 94), 180(94), 193(93, 94), 218, 286(94), 314
 Kraemer, J. M., 111(84), 112(84), 116(84, 92), 119(92), 120(84), 121(84), 135(92), 140
 Kraus, C. A., 49(23), 86
 Kreiler, C. G., 307(156), 315
 Kreiter, C. G., 261(55), 313
 Krespan, C. G., 60(57), 86, 167(78), 168(78), 202(147), 203(147), 207(147), 211(147), 218, 220
 Kriebitzsch, N., 315
 Kriebie, R. H., 53(42), 86
 Krieger, M., 286(97), 314
 Kritskaya, I. I., 286(76), 313
 Krüerke, U., 3(8), 39(8), 40(8), 41(128), 43, 46
 Kuivila, H. G., 49, 50(32a, 35), 51(26, 27, 28, 29, 35), 58(56), 61(60), 66(63, 64), 69(63), 71(56), 72(56), 73(56), 74(56), 76(56), 77(56), 78(56), 80(32a), 83(26, 27, 28), 84(28), 86, 87, 168, 169(77), 218

Kumada, M., 107(68, 72), 134(68), 139, 140
 Kupchik, E. J., 74(75), 85(82), 87
 Kurnosova, P. U., 300(119), 314
 Kursanov, D. N., 258(47), 312
 Kuzel, P., 315
 Kwon, J. T., 167(78a), 168(78a), 218, 300(125), 314

L

Lacher, J. R., 148(12), 152(12), 216
 Lagowski, J. J., 153(45), 156(45), 178(89), 204(89, 150, 150a), 217, 218, 220
 Lancaster, J. E., 34(103), 36(110), 45
 Langseth, A., 291(107, 292(111), 295(111), 314
 Lanigan, T., 85(82), 87
 Lecomte, J., 241, 251(21), 257(21), 312
 Leebrick, J. R., 151(25), 217
 Leermakers, P. A., 49(20d), 70(20d), 86
 Lemal, D. M., 18(57), 19(57), 44
 Lesbre, M., 48(14), 51(14), 85(84), 85, 87
 Leto, J. R., 3(9), 39(9, 125), 43, 46, 286(92), 314
 Levine, M., 151(22), 216
 Levine, R., 164(70), 218
 Li, W.-K., 152(32), 217
 Lichtenwalter, G. D., 106(56, 58, 62, 64), 139
 Lide, D. R., Jr., 48(13), 51(13), 85
 Lindner, E., 179(100, 101), 185(100), 188(100, 101), 189(100, 101), 193(101), 218, 219
 Lindsey, R. V., Jr., 108(80), 140
 Linn, W. J., 203(148a), 207(148a), 220
 Lippincott, E. R., 18(51), 22(51), 44, 241(16, 17), 251(17), 252(17), 257(17), 266(16, 17), 274(17), 277(62), 302(133, 134), 303(134), 304(141), 307(17), 309(17), 311(158), 311, 313, 315
 Lipscomb, W. N., 5, 9(14), 13(14), 23(13, 14, 15), 43, 306(144a, 145, 146), 307(146, 150), 315
 Liu, S. L., 102(45), 139
 Livingstone, J. G., 204(151), 205(151), 220
 Löchner, A., 315
 Lokshin, B. U., 286(76), 313
 Lord, R. C., 291(107), 304(141), 314, 315

Lorenz, D. H., 70(73), 74(76), 87
 Lucken, E. A. C., 19, 44
 Luijten, J. G. A., 48(16), 49(22), 51(16, 39), 53(47, 48, 49), 54(48, 49), 55(49, 51), 56(53), 58(48), 59(48), 70(48), 74(48), 81(48), 85, 86
 Lüttke, W., 252(38), 257(38), 268(38), 274(38), 293(38, 113), 295(38), 296(38), 312, 314
 Luxmoore, A. R., 35(108, 109), 45

M

McBee, E. T., 146(7), 151(27, 28), 216, 217
 Macbeth, A. K., 68(69), 87
 McBride, D. W., 180(102a, 106, 107), 181(106), 184(102a), 185(102a, 123), 187(106), 188(102a, 106, 107, 123), 193(123), 198(102a, 123), 200(123, 143), 208(102a, 106, 123, 143), 211(102a, 123), 219, 220
 McClellan, W. R., 179(95), 183(95), 185(95), 187(95), 188(95), 189(95), 207(95), 208(95), 218
 McClevery, J. A., 280(65), 284(65), 285(65, 72a), 313
 McDonald, R. S., 304(141), 315
 McFarlane, W., 12(30, 31), 23(30), 31(30, 31, 92), 43, 45, 307(155), 315
 McGrath, T. F., 164(70), 218
 Maciel, G. E., 163(68), 218
 McKenna, J. F., 222(5), 237
 McKusick, B. C., 228(28), 229(30), 231(36), 238
 McLaughlin, D. E., 109(83), 140
 McNeill, E. H., 48(15), 51(15), 85
 McOmie, J. F. W., 261(53, 54, 55), 313
 Maginn, R. L., 286(94), 314
 Magnani, A., 232(41), 238
 Mahler, J. E., 12(32), 13(32), 15(32, 37), 29(32), 33(32, 37), 34(32), 43, 44
 Mair, R. D., 291(109), 314
 Maitlis, P. M., 184(120), 188(120), 219
 Manakov, M. N., 104(46a), 139
 Manastyrskij, S. A., 303(138), 315
 Manchot, J., 257(44), 293(44), 298(117), 299(44, 118), 300(123, 124), 301(123), 312, 314

- Manuel, T. A., 6(18, 19), 13(18), 15(34, 36), 16(34, 45), 17, 18(34), 21, 22(18, 19, 34, 64), 23, 25(36), 26(74), 27(74, 83), 28(19), 29(19, 34), 43, 44, 45, 178 (92), 180(92), 181(92), 187(92, 126), 190(92), 192(126), 193(126), 195(92), 208(92), 218, 219, 307(148), 315
- Mark, H., 98, 138
- Markby, R., 17(48, 49), 38(5), 37(116, 117), 38(5, 116, 117), 43, 44, 45, 197 (137), 219
- Marko, L., 250(32), 312
- Marsh, J. F., 156(51), 217
- Martin, G., 106(65), 139
- Mason, R., 199(142a), 208(142a), 220
- Massey, A. G., 150(19a, 19b), 156(19a), 158(19a), 172(19b), 174(19b), 184 (122), 187(122), 216, 219
- Mateescu, Gh., 261(54, 55), 313
- Mathews, F. S., 306(144a), 315
- Mathis-Noel, R., 48(14), 51(14), 85
- Matthies, M., 48(4), 85
- Maung, M. T., 204(150a), 220
- May, L., 48(11), 51(11), 85
- Meckbach, H., 90(4), 137
- Meier, R., 164(69), 218
- Meiners, A. F., 151(27, 28), 217
- Melby, L. R., 235(56), 238
- Menapace, L. W., 50(32a), 58(56), 71(56), 72(56), 73(56), 74(56), 76(56), 77(56), 78(56), 80(32a), 86
- Merenyi, R., 36(115), 41(128, 132), 42 (115, 132, 133), 45, 46
- Metzger, A., 223(10a), 237
- Mez, H. C., 258(50), 312
- Middleton, W. J., 203(148a), 207(148a), 220
- Miller, E. H., 151(25), 217
- Miller, F. A., 291(103, 110), 314
- Miller, J. J., 233(47), 238
- Miller, S. A., 240(2), 311
- Miller, W. T., 200(145), 201(145), 220
- Mills, J., 228(28), 238
- Mills, O. S., 3(6), 4, 23(70), 38, 43, 44, 45, 196(139), 220, 250(34), 258(50), 312
- Mizushima, S., 252(37), 312
- Moffitt, W., 258(48), 312
- Monchamp, R. R., 250(33), 312
- Moon, S., 286(77), 313
- Morehouse, E. L., 316
- Morris, J., 181(113), 187(113), 207(113), 219
- Morris, L., 227, 238
- Mortensen, J. P., 301(131), 315
- Morton, J., 222, 237
- Moser, H., 246(28), 252(28), 312
- Mosher, W. A., 223, 227(26), 237, 238
- Motz, K. L., 286(77), 313
- Mukherjee, R. N., 203(148), 220
- Mumford, F. E., 231(37), 238
- Munro, J. D., 303(139), 315
- Murdoch, H. D., 34, 36(110), 45
- Murray, A. G., 117(98), 140
- Murray, J. G., 316
- Murray, M. J., 241(18), 311
- Musgrave, W. K. R., 204(151), 205(151), 220

N

- Nagy, P. L. I., 33, 35, 45
- Nakajima, J., 107(72), 140
- Nakamura, A., 6(20), 16(44), 18(44), 22 (20, 44), 23(20), 43, 44, 307(153), 315
- Nakamura, H., 316
- Nefedov, O. M., 104(46a), 139
- Nelson, R. D., 241(16, 17), 251(17), 252 (17), 257(17), 266(16, 17), 274(17), 302(133), 307(17, 62), 309(17, 62), 311(158), 311, 315
- Nenitzescu, C. D., 261(54, 55), 313
- Nesmeyanov, A. N., 29(87), 45, 240(4), 286(76, 78), 311, 313
- Neumann, W. P., 49(18, 19, 20, 20a, 21), 50(18, 33, 34), 51(19, 21, 34), 52, 56 (20), 57(21), 58(21), 60(21), 61(21), 70(20, 20a), 85, 86, 91(6b, 6c), 99(6b), 138
- Neuse, E. W., 286(99), 314
- Newlands, M. J., 162(66), 163(66), 218
- Nicholls, B., 13, 44
- Nichols, L. D., 26(74), 27(74), 44
- Nield, E., 153(43), 217
- Niermann, H., 49(19, 20, 21), 51(19, 21), 52, 56(20), 57(21), 58(21), 60(21), 61 (21), 70(20), 85, 86
- Nikanishi, M., 224, 238
- Nist B. J., 258(46), 312
- Noack, K., 11(29), 43
- Nöth, H., 284(73), 285(73), 313

Noltes, J. G., 48(16), 49(22), 51(16, 37, 39), 53(47, 48, 49, 50), 54(48, 49), 55(49, 50, 51, 61), 56(49, 52, 54), 58(48, 49), 59(37, 48, 49, 54), 60(49, 61), 61, 62(37, 59, 61), 63(59), 65(49), 67(66), 70(48), 74(48, 66), 75(66), 81(48), 85, 86, 87
 Normant, H., 151(24), 217
 Nygaard, E. M., 221, 237

O

Orgel, L. E., 35(107), 45, 240(14), 311
 Overbaugh, S. C., 224, 238

P

Palm, C., 21(63), 44
 Paneth, F., 47, 48(1, 3, 4), 85
 Park, A. J., 150(19a), 156(19a), 158(19a), 184(122), 187(122), 216, 219
 Park, J. D., 148(12), 152, 216
 Parshall, G. W., 35(105), 45, 196(134), 219, 235(57), 238
 Parsons, T. D., 154(48), 217
 Pass, F., 91(9), 138
 Patton, H. W., 101(44), 139
 Pauson, P. L., 2, 6(21), 14(4), 15(4), 23(21, 70), 24(21), 25(72), 43, 44, 196(131), 199(131), 219, 240(3), 286(80), 303(139), 311, 313, 314, 315, 316
 Peacock, R. D., 167(77a), 172(77a), 218
 Pepinsky, R., 240(12), 311
 Perevalova, E. G., 240(4), 311
 Pereyre, M., 69(71), 87
 Peterlik, M., 286(86, 87, 88), 313
 Peters, E., 153(41), 161(41), 217
 Peterson, D. J., 92(17, 18), 98(34), 99(18, 35), 106(59), 107(17), 110(17, 18, 34, 35), 113(34), 115(17, 18), 116(17, 18), 117(17, 35), 118(34), 119(17), 125(17, 18), 127(18), 129(18), 134(18), 135(17, 18, 34, 35), 136(34), 137(17), 138, 139
 Petro, A. J., 107(74), 140
 Petrov, A. D., 104(46a), 139
 Pettit, R., 10(25), 12(32), 13(32), 14(41, 42), 15(32, 37, 43), 16(42), 17(41, 50), 18(42, 53), 19(42, 53, 55), 28(43), 29(32), 31(93), 33(32, 37), 34(25, 32, 42, 50), 35(42), 43, 44, 45
 Petzold, R., 92(19a), 138
 Pfab, W., 311

Pfeiffer, P., 223(8), 237
 Pfrengle, O., 2(1), 15(1), 18(1), 43
 Phillips, C. S. G., 90(3), 91(3), 137
 Phillips, J. R., 153(46), 155(50), 166(46, 73), 167(46), 169(46, 73), 170(46), 171(46), 174(46), 181(111), 188(111), 214(46), 217, 218, 219
 Pierce, O. R., 146(7), 151(22, 27), 216, 217
 Pietrusza, E. W., 52(41), 53(41), 86
 Pinkina, L. N., 148(13), 152(13, 33, 34, 35), 153(34, 35, 36), 163(33), 216, 217
 Piper, T. S., 23(69), 44, 282(69), 284(70, 71), 288(100), 290(100), 313, 314, 316
 Pitcher, E., 179(97), 180(102a, 106), 181(97, 106, 110), 182(97), 184(102a), 185(102a), 187(97, 106, 119), 188(102a, 106, 107, 119), 189(97), 190(97), 191(97), 192(97), 200(143), 206(97, 153), 207(97, 113, 119, 153), 208(102a, 106, 110, 119, 143, 153), 209(110), 210(119), 211(102a, 119), 214(97, 155), 216(155), 218, 219, 220
 Plesske, K., 286(91, 96, 98), 314
 Plowman, R. A., 34(104), 45, 180(106), 181(106), 187(106, 125), 188(106, 125), 192(125), 193(125), 208(106), 219
 Plumb, J. B., 162(66), 163(66), 218
 Polo, S. M., 107(77), 140
 Pommier, J. C., 49(20b, 20c), 70(20b, 20c), 85, 86
 Poole, H. G., 291(106), 295(106), 314
 Powell, H. B., 204(150a), 220
 Pratt, L., 5(12), 12(12, 31), 14(40), 15(12), 18(54), 19(54), 21(40), 22(40), 25(73), 26(73), 31(31, 40, 92), 41(54), 42(54), 43, 44, 45, 181(112), 188(112), 195(112), 196(112), 199(112), 200(112), 208(112), 216(112), 219, 280(65), 284(65), 285(65), 299(118a), 307(155), 313, 314, 315, 316
 Priebe, E., 298(117), 314
 Pruett, R. L., 200(143), 208(143), 220, 316
 Pummer, W. J., 153(40, 41, 42), 161(41, 42), 217

R

Raab, G., 148(15, 16), 149(16), 153(38, 39), 167(39), 172(16, 39), 213(39), 216, 217
 Rabinowitsch, E., 48(3), 85

- Racky, G., 107(73), 140
 Radecki, A., 133(107), 141
 Radionov, A. N., 277(60), 313
 Ramsden, H. E., 151(25), 217
 Randall, E. W., 150(19b), 172(19b), 174
 (19b), 206(153a), 216, 220
 Ranning, J., 107(73), 140
 Rao, R. S., 68(68), 87
 Raskin, Sh. Sh., 300(120, 121, 123b), 314
 Rausch, M. D., 22(66), 23(66), 44, 286(89,
 90), 313
 Razuvayev, G. A., 99(36), 139
 Rebaudo, R., 286(95), 314
 Reed, H. W. B., 198(140a), 220
 Reeder, J. A., 77(78), 87
 Reeves, L. W., 207(152), 220
 Reihlen, H., 2, 15(1), 18, 43
 Reitsema, R. H., 68(70), 87
 Reppe, W., 2, 37, 43
 Reuter, H., 92(19a), 104(47), 138, 139
 Reynolds, L. T., 252(39), 277(39), 279
 (39), 312
 Richards, J. H., 284(72), 286(72), 313
 Richardson, R. D., 152(31), 217
 Riemschneider, R., 286(93, 97), 314
 Rigaudy, J., 222(3), 237
 Rinehart, K. L., Jr., 286(77, 82, 83), 313
 Roberts, C. W., 151(28), 217
 Roberts, J. D., 10(26), 43
 Robinson, G., 4, 43, 250(34), 312
 Rochow, E. G., 53(44), 86, 162(63, 64),
 172(85), 218
 Rohwedder, K. H., 154, 217
 Rosenberg, S. D., 151(25), 171(82), 217,
 218
 Rosenblum, M., 284(72), 285(74, 75), 286
 (75, 79, 81), 313
 Rosenthal, W., 234(51), 238
 Rosenwald, R. H., 224, 226, 238
 Rothman, L. A., 75(77), 78(77), 87
 Rubalcava, H. E., 286(84), 313
 Ruch, E., 292, 314
 Rundle, R. E., 300(123a), 314
 Russell, P. B., 236(58), 238
 Ryan, M. T., 104(46), 139
 Sandorfy, C., 251(35), 312
 Sands, J. E., 92(13), 94(13, 25), 95(13),
 96(13), 97(13), 106(25), 110(13),
 113(13), 116(13), 119(13), 120(13),
 123(13), 127(13), 129(13), 135(13),
 138
 Sauer, R. J., 232(42), 238
 Savory, J., 148(17), 216
 Sawyer, A. K., 49, 50(35), 51(26, 27, 28,
 29, 35), 70(72), 83(26, 27, 28), 84(28),
 86, 87
 Schaeffer, G. W., 48(6), 85
 Schenck, G. O., 36(112), 45
 Schindlbauer, H., 91(9), 138
 Schlenk, W., 98, 107(73), 138, 140
 Schlesinger, H. J., 48(9), 51(9), 85
 Schlögl, K., 286(85, 86, 87, 88), 313
 Schmidlin, J., 223, 237
 Schneider, R., 274(59), 290(101), 298(117),
 313, 314
 Schomaker, V., 40(127), 46, 258(49), 312
 Schott, G., 91(7), 106(66), 129(66), 138,
 139
 Schrauzer, G. N., 3(7), 15(39), 20(61), 22
 (66), 23, 31(91), 39, 40(7, 39, 124),
 41(7, 39), 43, 44, 45, 46
 Schwarz, N. V., 38(120), 45
 Schwarz, R., 90(4), 91(11), 137, 138
 Schwebke, G. L., 101(41, 43, 44), 103(41),
 104(41), 105(41), 113(41), 114(41,
 89), 115(41), 116(41, 92, 94), 119(92,
 94), 120(94), 125(41, 94), 126(41),
 127(41), 130(41), 131(41), 132(41,
 105), 134(41), 135(41, 92), 136(41),
 139, 140, 141
 Searles, S., Jr., 109(83), 140
 Seffl, R. J., 148(12), 152(12), 216
 Seiler, H., 286(85, 87), 313
 Senter, J. O., 284(72), 286(72), 313
 Serée de Roch, 48(14), 51(14), 85
 Severin, T., 232(43), 238
 Seyferth, D., 72(74), 73(74), 85(83), 87,
 148(11, 15, 16), 149(16), 153(38, 39),
 161(60), 163(60, 68), 164(60), 165
 (60), 167(39), 170(79), 172(11, 16, 39,
 79, 83, 84, 85), 192(11), 207(60, 68),
 211(60), 213(39), 216, 217, 218
 Shaefer, O. A., 291(108), 314
 Shanon, J. S., 68(69), 87
 Sharkey, W. H., 203(148a), 207(148a), 220

S

- Saggiomo, A. J., 159(58), 160(58), 217
 Saitow, A., 172(85), 218

- Sharp, D. W. A., 28(86), 40(86), 45, 183
(118), 188(118), 191(118), 196(135,
136), 198(136), 199(136), 208(136),
219
- Shaw, B. L., 176, 182(116), 190(116), 193
(87), 196(132), 198(140a), 200(132),
218, 219, 220
- Shaw, D., 150(19b), 172(19b), 174(19b),
216
- Shealy, Y. F., 230(31), 238
- Shearer, H. M. M., 258(50), 312
- Sheppard, N., 261(53, 54, 55), 313
- Sherer, P. C., 49(24), 86
- Shigorin, D. N., 277, 313
- Shiina, K., 107(72), 140
- Shim, K. S., 18(57), 19(57), 44
- Sicher, J., 107(76), 140
- Sim, S. Y., 125(103), 140
- Simmons, D. E., 48(15), 51(15), 85
- Sly, W. G., 197(138), 219
- Smith, A. G., 106(52, 54), 107(54), 133
(106a), 134(52), 139, 141
- Smith, D. L., 7, 9(23), 41, 43, 196(133),
198(133), 199(133), 219
- Smolin, E. M., 58(55), 59(55), 66(55), 86
- Smyth, C. P., 107(74), 140
- Snyder, R. G., 293(115), 295(115), 314
- Sokol, P. E., 286(83), 313
- Somieski, C., 91(12), 138
- Sommer, L. H., 52(41), 53(41), 86, 108
(78, 81), 109(81), 126(81), 140
- Sommer, R., 49(20, 21), 51(21), 56(20, 21),
57(21), 58(21), 60(21), 61(21), 85, 86
- Spangler, F. W., 229(30), 238
- Speck, S. B., 229(29), 232(44), 238
- Spielman, J. R., 51(40), 86, 171(81), 218
- Stafford, S. L., 15(36), 25(36), 27(83), 44,
45, 148(14), 152(14), 153(14, 37), 156
(53, 54), 157(53, 55, 56), 163(55), 165
(55, 56), 167(37), 170(37), 172(37, 54),
178(92), 179(99), 180(92, 99, 107),
181(92, 110), 184(99), 187(92, 99),
188(99, 107, 110), 190(92, 99), 191
(99), 195(92), 207(56), 208(92, 110),
209(110), 212(55, 56), 213(37, 54, 55),
216, 217, 218, 219
- Stammreich, H., 241, 251(19), 252(19,
38), 255(43), 257(38), 266, 267, 268,
274(38), 281(66), 293(38), 295(38),
296(38), 311, 312, 313
- Stanley, R. R., 101(42), 139
- Stark, K., 36(110), 45
- Steele, A. R., 92(15), 98(15), 110(15), 135
(15), 138
- Steele, D., 277(62), 307(62), 309(62), 313
- Steele, W. C., 107(75), 140, 162(65), 218
- Stephens, R., 149(19), 150(19), 153(43),
216, 217
- Sterlin, R. N., 148(13), 152(13, 30, 32, 33,
34, 35), 153(34, 35, 36), 163(33), 216,
217
- Stern, A., 51(38), 59(38), 86
- Sternberg, H. W., 3(5), 17(48, 49), 24(71),
37(116, 117), 38(5, 116, 117), 43, 44,
45, 190(128), 197(137), 219
- Steudel, W., 106(60), 113(86), 134(86),
139, 140
- Stevens, P. G., 230, 238
- Stock, A., 90, 91(2, 12), 106(2), 137, 138
- Stokes, C. S., 159(58), 160(58), 217
- Stone, F. G. A., 6(18, 19), 13(18), 15(34,
36), 16(34, 45), 18(34), 21, 22(18, 19,
34, 64, 65), 23, 25(65), 26(74, 76), 27
(74, 76, 83, 84), 28(19, 34), 29(19, 34),
43, 44, 45, 90(5), 107(75), 137, 140,
148(10, 14), 150(19a, 19c), 152(14,
29), 153(14, 37, 46), 155(49, 50), 156
(19a, 52, 53, 54), 157(53, 55, 56), 158
(19a), 162(65), 163(55), 165(55, 56),
166(46, 73), 167(29, 37, 46), 168(29),
169(46, 73), 170(29, 37, 46), 171(29,
46, 80), 172(37, 54, 80), 174(46), 178
(91, 92), 179(91, 97, 98, 99), 180(91,
92, 99, 102, 102a, 105, 106, 107), 181
(92, 97, 98, 106, 110, 113), 182(97,
117), 183(91, 117, 119), 184(99, 102a,
120, 122), 185(102a, 123a), 187(91,
97, 98, 99, 106, 113, 117, 119, 122,
123a, 125), 188(91, 98, 99, 102a, 105,
106, 107, 110, 119, 120, 123a, 125),
189(91, 97, 102), 190(92, 97, 99),
191(97, 99, 123a), 192(10, 97, 125),
193(125), 195(92), 200(143), 206(97,
153), 207(56, 97, 113, 119, 153), 208
(92, 102a, 106, 110, 119, 143, 153),
209(110), 210(119), 211(102a, 119),
212(55, 56), 213(37, 54, 55), 214(46,
97, 155), 216(155), 216, 217, 218, 219,
220, 303(137), 307(148), 315, 316
- Streitwieser, A., Jr., 79(79), 87

Strycker, S. J., 230(32), 238
 Szwarc, M., 79(80), 87

T

Takamizawa, M., 85(83), 87
 Taketa, A., 107(68), 134(68), 139
 Talalaeva, T., 277(60), 313
 Tamaru, K., 48(10), 85
 Tamborski, C., 104(46), 139
 Tamres, M., 109(83), 140
 Tarama, K., 107(68), 134(68), 139
 Tarrant, P., 148, 152(31), 216, 217
 Tatlow, J. C., 149(19), 150(19), 153(43),
 167(77a), 172(77a), 216, 217, 218
 Taufen, H. J., 241(18), 311
 Tebboth, J. A., 240(2), 311
 Tengler, H., 179(96), 187(96), 218
 Thiel, M., 18(51), 22(51), 44
 Thiele, J., 263, 313
 Thompson, H. W., 304(140), 315
 Thompson, P. G., 153(45), 156(45), 217
 Thomson, J. B., 286(84), 313
 Tilney-Bassett, J. F., 196(139, 140), 220
 Tomasi, R. A., 105(49, 49a), 106(49a), 113
 (49), 114(49a), 115(49a, 90a), 116
 (49a, 96), 118(96), 123(96), 124(49a),
 125(49a), 126 (49a, 90a, 104), 129(95),
 130(90a), 132(49), 133(49), 134(49,
 90a), 135(49a, 104), 136(49a, 90a),
 139, 140
 Tombouljian, P., 223(10a), 227(25), 237,
 238
 Treichel, P. M., 26(76), 27(76, 84), 44,
 45, 150(19c), 152(29), 167(29), 168
 (29), 170(29), 171(29), 179(97, 98,
 99), 180(99, 105, 106), 181(97, 98, 106,
 113), 182(97, 117), 183(117), 184(99,
 122), 185(123, 123a, 124), 187(97, 98,
 99, 106, 113, 117, 122, 123a), 188(98,
 99, 105, 106, 123a), 189(97), 190(97,
 99), 191(97, 99, 123a), 192(97), 206
 (97), 207(97, 113), 208(106, 110), 209
 (110), 214(97), 216, 217, 218, 219, 316
 Tremaine, J. F., 240(2), 311
 Tresselt, L. W., 307(152), 315
 Trifan, D. S., 286(99), 314
 Truter, M. R., 35(108, 109), 45
 Tsuchida, R., 316
 Tull, R., 230(35), 238

U

Ulm, K., 315, 316

V

Vago, E. E., 304(140), 315
 Valade, J., 49(20b, 20c), 69(71), 70, 85, 86,
 87
 van der Kerk, G. J. M., 48(16), 49(22), 51
 (16, 37, 39), 53(47, 48, 49), 54(48, 49),
 55(49, 51, 61), 56(49, 52, 53, 54), 58
 (48, 49), 59(37, 48, 49, 54), 60(49, 61),
 61(59), 62(37, 59, 61), 63(59), 65(49),
 67(66), 70(48), 74(48, 66), 75(66), 81
 (48), 85, 86, 87
 Vaubel, W., 48(2), 85
 Vdovenko, V. M., 48(7), 85
 Veer, W. L. C., 234(54), 238
 Veltman, P. L., 2(3), 43
 Ventura, J. J., 48(17), 85
 Vetter, H., 2, 37, 43
 Villiger, V., 231, 238
 Volpin, M. E., 258(47), 312
 von Christiani, A. F., 234(50), 238
 von Hessling, G., 2(1), 15(1), 18(1), 43
 Vyazankin, N. S., 99(36), 139

W

Wada, T., 148(15), 161(60), 163(60, 68),
 164(60), 165(60), 207(60, 68), 211(60),
 216, 217, 218
 Wailes, P. C., 3(10), 37(10), 38(10, 123),
 43, 46
 Walaschewski, E. G., 200(144), 201(144),
 220
 Walburn, J. J., 151(25), 217
 Walker, G. D., 301(127), 314
 Wall, L. A., 153(40, 41, 42), 161(41, 42),
 217
 Walsh, E. J., 50(32), 51(32), 52(32), 56
 (32), 72(32), 73(32), 74(32), 78(32),
 81(32), 82, 86
 Walter, J., 243(23), 244(23), 246(23), 312
 Wampler, D. L., 41(131), 46
 Warner, C. R., 58(56), 71(56), 72(56), 73
 (56), 74(56), 76(56), 77(56), 78(56), 86
 Waser, J., 91(10), 138
 Watterson, K. F., 27(81, 82), 28(81, 85),
 45, 181(109, 112), 187(109), 188(112),
 193(109, 112, 130), 196(112), 199

- (112), 200(112), 208(112), 216(112), 130), 219
- Weatherbee, C., 233(46), 238
- Weber, S., 84(81), 87
- Weeks, E. J., 48(5), 85
- Weiner, M. A., 172(83), 218
- Weinhouse, S., 230, 238
- Weiss, E., 3(8), 26(75), 27(77), 34, 36, 39 (8), 40(8), 41, 42, 43, 44, 45, 46, 199 (142), 220, 293(116), 314
- Welch, D. E., 148(16), 149(16), 172(16), 216
- Wender, I., 3(5), 17(48, 49), 24(71), 36 (116, 117), 38(5, 116, 117), 43, 44, 45, 190(128), 197(137), 219
- Werner, R. P. M., 303(138), 315
- Wertheim, G. K., 7(22), 43
- West, R., 108(79), 140, 277(61), 313
- West, R. C., 53(44), 86
- Weyenberg, D. R., 108(81), 109(81), 126 (81), 140
- Whiffen, D. H., 291(105), 314
- Whitcomb, S. E., 254(40), 266(40), 268 (40), 312
- Whiting, M. C., 3(10), 13, 37(10), 38(10, 120, 121, 122, 123), 43, 44, 45, 46
- Whitmore, F. C., 52(41), 53(41), 86
- Whyman, D., 146(8), 147(9), 161(9), 167 (9), 168(9), 216
- Wiberg, K., 258(46), 312
- Wilford, J. B., 182(117), 183(117), 187 (117), 219
- Wilkinson, G., 5(12), 10(28), 12(12, 30, 31), 14(40), 15(12), 18(52, 54), 19(52, 54), 21(40, 52), 22(40), 23(28, 30, 69), 24(28), 25(52, 73), 26(52, 73), 27(81, 82), 28(81, 85, 86), 31, 35(105), 40 (86), 41, 42(54), 43, 44, 45, 181(109, 112), 187(109), 188(112), 195(109, 112, 130), 196(112, 134, 135, 136), 198(136), 199(112, 136), 200(112), 208(112, 136), 216(112, 130), 219, 240 (6), 254(41), 279(64a), 280(65), 281 (66, 67), 282(69), 284(65, 70, 71), 285 (65, 72a), 288(100), 290(100), 299 (118a), 307(155), 311, 312, 313, 314, 315, 316
- Williams, R. O., 18(58), 19(58), 44
- Willis, C. J., 157(57), 158(57), 165(72), 166(72, 74, 75), 167(75), 169, 171(57, 75), 207(152, 154), 217, 218, 220
- Wilson, C. L., 291(106), 295(106), 314
- Wilson, E. B., Jr., 247(29), 255, 291(29), 292(29), 297, 299, 312
- Wilson, G. R., 133(106a), 141
- Wilson, M. K., 107(77), 140
- Wilzbach, K. E., 48(9), 51(9), 85
- Winkhaus, G., 31(90), 45, 299(118a), 314
- Winkler, H. J. S., 92(17, 18), 94(26), 97 (29), 98(33), 99(18, 35), 106(26, 33, 61), 107(17), 110(17, 18, 35), 111(84), 112(84), 113(26), 114(85), 115(7, 18, 91), 116(17, 18), 117(17, 35, 85), 118 (91), 119(17), 123(29), 125(17, 18), 126(91), 127(18, 29), 129(18), 134 (18, 26), 135(17, 18, 29, 35), 137(17), 138, 139, 140
- Winter, W. K., 254(40), 266(40), 268(40), 312
- Wittenberg, D., 98(33), 106(33, 51, 56, 59, 64), 138
- Wohl, J., 223, 237
- Wood, J. S., 298(116a), 314
- Wotiz, J., 197(137), 219
- Wu, T. C., 98(33), 106(33, 50, 52, 53, 55), 107(55, 71), 134(52, 55), 138, 139, 140
- X
- Xavier, J., 18(51), 22(51), 44, 277(62), 307 (62), 309(62), 313
- Y
- Yamada, S., 316
- Yamaguchi, M., 107(72), 140
- Yamamoto, Y., 107(72), 140
- Yamazaki, H., 72(74), 73(74), 87
- Yatsenko, R. D., 148(13), 152(13, 30, 33, 34, 35), 153(34, 35, 36), 163(33), 216, 217
- Yeldel, J. B., 48(15), 51(15), 85
- Young, J. C., 161(61), 163(67), 191(67), 218
- Z
- Zahn, U., 315
- Zeise, W. C., 240, 311
- Zeiss, H. H., 240(7), 301(129), 311, 315, 316
- zu Stolberg, U. G., 132(105a), 133(106), 134(106), 135(106), 141

SUBJECT INDEX

A

- Acetylenes, reaction with organotin hydrides, 62, 63, 65
- Acetylene-Fe carbonyl complexes, 37, 38, 41, 42
- Acyclic diene $\text{Fe}(\text{CO})_3$ complexes
 - cationic configuration, 33
 - NMR, 12
 - preparation, 18
- Acyl halides, reduction by organotin hydrides, 79, 81–82
- 1,2 Addition, Grignard, 221–223
 - to mesityl ketones, 228–229
 - to polycyclic ketones, 227
- 1,3,5, Addition, Grignard, 232
- 1,4 Addition, Grignard, 221–223
 - aromatic-heterocyclic ketones, 233–235
 - mesityl ketones, 228–230
 - to polycyclic ketones, 224
 - quasi-6-membered ring, 224–225
- 1,6 Additions, Grignard
 - Fuchsone type ketones, 231–232
 - mesityl ketones, 228–229, 231
 - to polycyclic ketones, 228
- Addition mechanism, organotin hydrides, 63–65, 71
- Alkali metal carbonylmetallate
 - reaction with perfluoroallyl chloride, 183–184
 - with perfluoroacyl halide, 178–180
- Alkyl halide, reduction with organotin hydride, 70–80
- Alkyne-iron carbonyl complexes, 37–43
- Allyl cations, iron carbonyl complexes, 3–4
- Allyl halides, reaction with iron carbonyls, 34
- Anil, 223
- Anti-Stokes lines, 242
- Aromatic heterocyclic nitrogen compounds, conjugate addition, 233
- Aryl halides, reduction with organotin hydride, 70–80

B

- Benzene-metal complexes, 291–302
 - analysis of benzene spectra, 291–292

Benzene-metal complexes—*cont.*

- benzene-metal carbonyls, 299–301
- dibenzene-metal complexes, 256, 293–299, 310
 - substituted benzene complexes, 301–320
- Bicycloheptadiene, substituted complexes, 18–19, 28
- Bond cleavage, Si—Si bond
 - by bases, 106
 - by halogens, 107
 - by organometallic reagents, 106
 - mechanism, 107–110
- Bond stability, thermodynamic
 - of perfluoroalkyl-lithium compounds, 153
 - of perfluoroalkyl-tin compounds, 154
 - of perfluoroalkyl-transition metals, 154
- Bond strength
 - alkyl tin hydrides, 64
 - aryl tin hydrides, 64
- Butadiene iron tricarbonyl, 2–5, 12, 29

C

- Carbonium ion type ligands, 3, 4, 11, 30, 31, 33, 34, 35
- Carbonyl absorption, infrared, of diene-iron complexes, 11, 30
- Carboxylic acids, reduction with organotin dihydrides, 82–84
- Catenation, of carbon, 90
 - of group IVb elements, 90–91
 - of tin hydrides, 50
- Cationic ligands, 3, 4, 10, 11, 30–31, 33–35
- Character tables, 243–244
- Cyclic hydrocarbons, IR and Raman spectra, 254–255
- Cyclooctatetraene-iron carbonyl complexes
 - diiron hexacarbonyl, 5, 6
 - iron tricarbonyl, 5–6, 12–13, 20, 22–23, 28–29, 31
- Cyclooctatetraene-metal complexes, spectral studies 306–307
- Cyclooctatetraenyl anion, spectral studies, 304–306
- Cyclopropenium cation, 240
 - spectra analysis, 257–258

- Cyclopentadiene iron carbonyl derivatives, 23–25
dienyl-iron carbonyl cation, 31–33
reaction with fulvene, 36
- Cyclopentadienyl, spectral expectations, 262–264
- Cyclopentadienyl complexes, spectral analysis, 256–257
- Cyclopentadienyl metal carbonyls, spectral studies, 281–284
- Cyclopentadienyl-metal complexes
cyclopentadienyl anion, 262–263, 275
dicyclopentadienyls, 263–269, 270–272, 276–282, 309
identifying Cp–M bond type, 289–291
monocyclopentadienyls, 269, 275–278, 281–283
parameters affecting spectra, 286–289
spectral analysis of C₅ systems, 259–291
tetracyclopentadienyls, 273–274
tricyclopentadienyls, 272–273, 283
- Cyclopentadienyl metal hydrides, spectral studies, 284, 285
- Cyclopentadienyl nitrosyls, 284
- Cyclopentadienyls, ring substituted, spectra, 284–286
- Cyclosilanes
chemical properties, 115–116, 136
nomenclature, 93–94
perphenylated, 94–103, 117–132
physical properties, 94
preparation, 94, 110–115
- D**
- Deformation vibrations, 243, 248–251
- Diamagnetism
of fluorocarbon π -complex, 197, 199, 200
of π -bonded fluorocarbon transition metals, 195
- Diels-Alder adducts, 18, 20, 23
- Diene, reaction with organotin hydrides, 62, 63
- Diene-iron bonding, 3
- Diene-iron carbonyl complexes, 1–43
acyclic dienes, 12, 18, 33
conjugated complexes, 14–18
conjugating ability, 9–10
NMR studies, 12–13
nonconjugated complexes, 8, 9, 11, 18–20
- Diene-iron carbonyl complexes—*cont.*
preparation, 13
structure, 2, 4–10
X-ray studies, 4–10
- Dienyl-iron tricarbonyls
cationic reaction in cyclic system, 30–31
cis and *trans* forms, 33
chemical reactions, 29
cyclopentadiene, 31–33
displacement of ligands, 28–29
preparation, 13
reaction in acyclic systems, 33–34
 σ - and π -bonded complexes, 33
- Disilanes
alkyl disilanes, 129–130
aryl disilanes, 106, 109, 110
cleavage of Si–Si bond, 106–107
nomenclature, 93
properties, 134
reactions, 115, 136
- Diynes, reaction with organotin hydrides, 62–63
- Doppelkegel structure, 240–241, *see also* Sandwich structure
- E**
- Effective atomic number, 177
- Electrophilic cleavage series, 170, 205
- Enamine, 222
- F**
- Ferrocene, 1, 24
frequency assignment, 266–267
 π -bonding, 3
- Fluorine shift, in fluoroalkylboron compounds, 155–156
- Fluoroalkenyl, transition metal compounds
preparation, 178–186
properties, 186–195
- Fluoroalkyl, transition metals, 169
- Fluorocarbanion, 146
- Fluorocarbon derivatives of metals, 143–220, *see also* Pentafluorophenyl derivatives, Perfluoroacyl derivatives, Perfluoroalkyl derivatives, Perfluorovinyl derivatives, Polyfluoroalkyl derivatives
- Free radical chain mechanism, organotin hydride additions, 63, 70, 75, 79, 80
- Fulvene-iron carbonyl complexes, 36–37, 42

G

- Geminal polyhalides, reduction by organotin hydrides, 71
Grignard reagents
 preparation from perfluorovinyl compounds, 152
 addition heterocyclic aromatic, 232–235
 addition of heterocyclic ketones, 233–235
 of mesityl ketones, 228–230
 of phenolic ketones, 235–236
 of polycyclic ketones, 223–228
 of unhindered ketones, 237
Group frequency, 243, 246

H

- Halobenzene, *p*-substituted, reduction with organotin hydride, 75
 α -Haloketones, reduction with organotin hydride, 74
Harmonic oscillator equation, 308
Heterocyclic aromatics, addition of Grignard reagents, 232–235
Hindered ketones
 conjugate addition to Grignard reagents, 228–232
 1,6 addition, 231
 p-alkylation, 229, 231
Hydride carrier, 80
Hydrogen migration, in diene-iron carbonyl complex, 14, 15, 42
 in triene complex, 21
Hydrogen transfer reaction, in triene-iron carbonyl complex, 21
Hydroperoxide, 229
Hydrostannation, 56, 63–65, 67, *see also*
 Organotin hydrides, chemical properties

I

- Infrared spectra, diene-iron carbonyl complex, 5, 10–11
Infrared spectroscopy, of π -complexes
 instrumentation, 251–252
 measurement in liquid phase, 253
 in solid state, 253–254
 in vapour phase, 252–253
Irreducible representations, 244–246, 249–251, 254
Iron carbonyl anion, 37–38
Iron tetracarbonyl complex, 14, 35–36

L

- Ligand displacement, iron carbonyls, 28, 29
Ligands, iron carbonyl complex, 1, 3–4, 10, 24

M

- “Mehrkugel” molecules, 255
Mesityl ketones, conjugate addition of Grignard, 228–230
Metal carbonyl hydrides, reaction with unsaturated fluorocarbons, 181–183
Metal carbonyls
 reaction with olefins, 181, 183, 184
 with perfluoroalkyl iodides, 180–181
Monoolefin-iron tetracarbonyls, 35–36
Mössbauer resonance, of iron carbonyl complex, 6, 7
 μ bonds, of olefin-transition metals, 195–197
9, 10 μ rule, 284–286
Mutual exclusion, rule, 249, 255

N

- Nonconjugated diene-Fe(CO)₃ complexes, 8–9, 11, 18–20

O

- Olefin-iron carbonyl complex, 2
 tetracarbonyl complex, 14
Organosilyllithium compounds
 from chlorosilanes, 98
 reaction with decaphenylcyclopentasilane, 129–130
Organotin dihydrides
 addition to olefins, 59–61
 preparation of cyclic organotin compounds, 61
 of polymeric organotin compounds, 62–63
 reduction of aldehydes and ketones, 67
 of ketosteroids, 68–69
 with carboxylic acids, 82–84
Organotin hydrides
 addition to alkenes, 53–65
 to alkynes, 56, 61–65
 decomposition, 51, 52
 history, 47
 IR spectra, 49, 50
 nomenclature, 47–48
 physical properties, 48–51

- Organotin hydrides—*cont.*
 reaction with carboxylic acids, 82–84
 with organic compounds, 52–85
 reduction of acyl halides, 81–82
 of aldehydes and ketones, 66–70, 82
 of alkyl and aryl halides, 70–80
 toxicity, 52
- P**
- Pentavalent configuration, of polysilanes,
 109, 137
- Pentafluorophenyl derivatives of
 boron, 145, 150, 158–159
 lead, 150
 lithium, 149–150, 158
 magnesium, 150, 204
 mercury, 150, 204–205
 tin, 150, 153, 159, 166, 167, 169, 172
 transition metals, 150, 178–188, 190–195
- Perfluoroacyl, transition metal derivatives,
 186, 189–195
- Perfluoroacyl halides, 178–180
- Perfluoroalkyl derivatives of
 aluminum, 160
 boron, 145, 154–156
 cadmium, 201
 germanium, 165–166
 Grignard reagents, 151
 iodides, 144, 145, 150–151, 180–181,
 184–186
 iron, 216
 lead, 166, 174, 203
 lithium, 144–147, 168
 manganese, 186–187, 191, 206, 214–215
 mercury, 144, 153, 201–205
 rhenium, 214–216
 silicon, 145, 161
 tin, 154, 162, 165–171, 180, 203
 transition metals, 145, 178–195, 203, 214–
 215
 zinc, 145, 147, 200–201
- Perfluoroalkyl chloride, reaction with alkali
 metal carbonyl metallates, 183–184
- Perfluoro- π -allylic metal complex, 196
- Perfluorocarbon-metal derivatives, infrared
 spectra, 212, 214–216
- Perfluoroethyltin compounds, 152
- Perfluoromethylmagnesium iodide, 150–151
- Perfluoroolefins, reaction with iron car-
 bonyls, 27–28
- Perfluoropropyltin compounds, 147
- Perfluoro-*n*-propylmagnesium iodide, 151
- Perfluorovinyl, derivatives of
 boron, 156–159, 170
 Grignard reagents, 152–153
 lithium, 148–149, 164–165
 magnesium, 149
 silicon, 164–165
 tin, 148, 152, 156–157, 164–167, 172–
 173
- Perfluorovinyl-metal derivatives
 infrared, 213–214
 liquid film spectra, 213
 NMR of As, B, Ge, Hg, Si, Sn, 211–212
- Peri ring, conjugate addition of Grignard,
 227
- Perphenylated cyclosilanes
 decaphenylcyclopentasilane, 125–130
 dodecaphenylcyclohexasilane, 130–132
 octaphenylcyclotetrasilane, 117–125
 structural studies, 94–102
- Phenolic ketones, conjugate addition of
 Grignard, 235–237
 tautomerism, 235–236
- π -allyl nickel complexes, 200
- π -complexes of cyclic hydrocarbons,
 analysis of spectra, 255–257
- π -complexes, between metals and C_nH_n ring
 C_3 system, 257–258, 260
 C_4 system, 258–259, 262
 C_5 system, 259–291
 C_6 system, 291–302
 C_7 system, 303–304
 C_8 system, 306–307
- pK_a values, of iron carbonyl-diene carboxy-
 lic acids, 13
- Polycyclic ketones, conjugate addition of
 Grignard, 223–228
- Polyfluoroalkyl, derivatives of
 lithium, 145
 magnesium, 145
 manganese, 186, 191, 206
 mercury, 202
 silicon, 161–163
 tin, 166–170
 transition metals, 181–182, 186–189,
 190–195, 214
- Polyfluorocarbon-metal derivatives, NMR
 of As, B, Ge, Hg, Si, Transition metal,
 Zn, 212

Polysilanes, cyclic
 decaphenylcyclopentasilane, 125–130
 dodecaphenylcyclohexasilane, 130–132
 octaphenylcyclotetrasilane, 117–125
 structural studies, 94–102

Polysilanes, linear
 nomenclature, 93
 preparation, 105
 properties, 133–136

Polytin dihydrides, 50

R

Raman effect, 242

Raman spectroscopy, of π -complexes
 instrumentation, 251–252
 liquid phase, 253
 solid state, 253–254
 vapor phase, 252–253

Rayleigh scattering, 242

Reduction mechanism, organotin hydrides,
 66, 69–70, 75–80, 82, 84

Reductive acylation, 81–82

Reihlen's structure, 3

Reppe's complex, 37, 41–42

Ring opening, cyclosilanes, 105, 108–109

Ring strain, cyclosilanes, 107, 137

S

Sandwich structure, of ferrocene, 240–241

Schönflies notation, 245, 243–246

Selection rules, 242–243, 248, 294, 296

Sidgwick effective atomic number, 177

Silyl radical species, 137

Silylenes, 91

Silyllithium compounds

 cleavage of cyclosilanes, 115, 117

 cleaving agent, 106

 from Compound "C", 102

 preparation, 106

Spectroscopic studies

 infrared, fluorocarbon metal compounds,
 212–216

Spectroscopic studies—*cont.*

 NMR, fluorocarbon metal compounds,
 206–212

 Stannane, *see* Organotin hydrides

 Stokes lines, 242

 Stretching vibrations, 243, 248–251

 Symmetry, elements, 243–246, 249–250
 of cyclic hydrocarbons, 254–255

 Symmetry operations, 244–246

T

Tetrafluoroethylene, reaction with metal
 carbonyls, 180

Tin hydrides, *see* Organotin hydrides

Transition metal halides

 reaction with fluorocarbon Grignard
 reagents, 184–186

 with fluorocarbon lithium reagents,
 184–186

Transmetallation reaction, perfluorovinyl-
 lithium, 148–149

Triene-iron carbonyl complexes, 20–22

Tropone-iron tricarbonyl complexes, 7, 8,
 42–43

Tropylium cation, vibrational spectrum,
 302–303

Trouton constant, fluoroalkylboron com-
 pound, 154

U

Unhindered ketone, addition of Grignard,
 237

V

Vibrational spectra

 bond strength, 308

 symmetry force constants, 309

 thermodynamic function, 311

Vicinal dibromide, reduction with organo-
 tin hydride, 73–74

Z

Ziese's salt, 240